

**California Environmental Protection Agency**



**Air Resources Board**

**Air Quality Impacts of the Use of Ethanol  
in California Reformulated Gasoline**

**Appendix B**

**Photochemical Modeling**

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## B-1. Introduction

This appendix describes the air quality simulations performed in support of the analysis of the potential impact on air quality caused by the phase-out of gasoline containing methyl *tertiary*-butyl ether (MTBE) and replacement by ethanol-based or non-oxygenated fuels. It is important to bear in mind that the model results for this study are being used in a relative, rather than absolute sense. That is, the model was used to estimate the change from 1997 MTBE gasoline to ethanol-containing and non-oxygenated gasolines in 2003, rather than to predict absolute values in 2003. The estimated changes were then used to adjust the base year (1997) air quality measurements to future (2003) concentrations, as described in Appendix C. The modeling community is in general agreement that models are best used in a relative sense.

In the sections that follow a brief description of the air quality model is presented together with the photochemical mechanism chosen. A description of the input files necessary to run each of the scenarios considered is presented, together with a summary of the results. A discussion of sensitivity simulations and model performance is included. An analysis of the sensitivity of ozone, PAN, and PPN under a wide variety of conditions was conducted with a box model.

## B-2. Photochemical Model Description

Photochemical air quality modeling is a primary tool for understanding the complex interrelationships among pollutants emitted and transported in a given area. Photochemical air quality models are computer models that represent the state-of-the-science understanding of how ozone and other secondary pollutants are formed and the relationship to the primary pollutants emitted by different source categories. They have been used to assess the effectiveness of air pollution control strategies to achieve the air quality standards. The Flexible Chemical Mechanism Version of the Urban Airshed Model (UAM-FCM) is an air quality model that has been used by ARB since 1995.

The UAM-FCM is an adaptation of the Urban Airshed Model (UAM) to provide flexibility in incorporating different Carbon Bond IV or SAPRC-type photochemical mechanisms into the UAM (Kumar *et al.*, 1995). The UAM has been the primary air quality regulatory model for ozone control strategy development. However, it has a hard-coded a version of the Carbon Bond IV photochemical mechanism, together with a unique algorithm to solve the set of differential equations representing the chemical transformations that is accurate, robust and fast. The algorithm was designed to take maximum advantage of the Carbon Bond IV features. The treatment of photolytic reactions in the UAM is also unique. All values for the photolytic reaction rates are hard-coded, and depend on the value of the NO<sub>2</sub> photolytic reaction rate. The hard-coded approach in the UAM makes it very difficult to study recent and more updated mechanisms, such as those developed by Dr. W.P.L. Carter at the University of Riverside. Any change or update in the Carbon Bond IV mechanism, photolytic rates, or the implementation of a different chemical mechanism requires changes to the UAM

code that need to be done by hand. However, the UAM-FCM can read a text file version of a mechanism and create program subroutines that are readily integrated with the model (Kumar *et al.*, 1995). Below we briefly describe the main aspects of the UAM and the UAM-FCM.

### B-2.1. Urban Airshed Model

Morris and Meyers (1990) provide a detailed description of the UAM. Only a brief summary is provided here. The UAM is a gridded 3-dimensional air quality model that can simulate the atmospheric physical and chemical processes that cause air pollution. The basic advection-diffusion equation is:

$$\frac{\partial C_i}{\partial t} + \frac{\partial(uC_i)}{\partial x} + \frac{\partial(vC_i)}{\partial y} + \frac{\partial(wC_i)}{\partial z} = \frac{\partial}{\partial x}(K_H \frac{\partial C_i}{\partial x}) + \frac{\partial}{\partial y}(K_H \frac{\partial C_i}{\partial y}) + \frac{\partial}{\partial z}(K_V \frac{\partial C_i}{\partial z}) + R_i + S_i + L_i \quad (\text{B-1})$$

The first term on the left-hand side of Equation (1) represents the time-varying concentration of pollutant  $i$ , and the last three terms on the left-hand side of Equation (1) represent advection. The first three terms on the right-hand side of Equation (1) represent turbulent diffusion,  $R_i$  are chemical reaction processes,  $S_i$  are emission source processes, and  $L_i$  correspond to losses by deposition. The other terms in Equation (1) are the horizontal and vertical wind speed components --  $u$ ,  $v$ , and  $w$  -- and the horizontal and vertical diffusivity coefficients,  $K_H$  and  $K_V$ . Equation (1) is solved for each pollutant and grid cell at each time step in the simulation. As designed, the UAM has hard-coded a version of the Carbon Bond IV (CB4) chemical mechanism. The CB4 version implemented in the UAM was last updated in 1993 by adding radical-radical interactions. The hard-coded approach to the atmospheric chemical mechanism used in the UAM prevents the implementation of newer and more up-to-date chemical mechanisms.

### B-2.2. Flexible Chemical Mechanism Version of the Urban Airshed Model

The UAM-FCM was developed under contract for ARB (Kumar *et al.*, 1995). The UAM-FCM has a software package (the FCM) that reads a text file describing the photochemical mechanism, and creates a set of mechanism-specific programs that are then integrated into the UAM. The FCM allows the user to incorporate reaction-specific photolytic rates, by providing a file for each photolytic reaction, with data on cross section and quantum yield for each wavelength of interest. The UAM-FCM has a generalized technique to solve the set of differential equations that is not mechanism specific, but is accurate and robust. The current version of the UAM-FCM can handle up to 220 chemical reactions (including up to 20 photolytic reactions), and up to 140 chemical species.

### B-2.3. SAPRC97 Chemical Mechanism

Carter (1993, 1997) developed the atmospheric chemical mechanism designated as SAPRC97 (version D), which is readily processed by the UAM-FCM software. To save computing time in solving the set of differential equations that represent the reaction mechanism, only a small number of hydrocarbon species are treated explicitly in this mechanism. In the SAPRC series of mechanisms, hydrocarbons are grouped together using the lumped-molecule approach. In this approach the reactions of many alkanes, alkenes, and aromatic species that are present in the emission inventory are represented by lumped reaction mechanisms (Carter, 1990). The computer software calculates the kinetic rates and product yield parameters for the lumped species that best represent the unique hydrocarbon mixture in the emission inventory (Carter, 1988; Carter 1990). For this study the one-product mechanism is used to represent the reactions of isoprene (Carter, 1996). In addition, explicit reaction mechanisms (as opposed to a lumped representation) for several compounds of interest (such as benzene, 1,3-butadiene, ethanol, and methyl *tertiary*-butyl ether) were added to the original version of the SAPRC97. It was also desired to distinguish between acetaldehyde and formaldehyde formed as by-products of photochemical reactions (secondary), from those emitted directly from sources (primary). The explicit reactions for the additional species were obtained from Dr. Carter's ftp site (<ftp://cert.ucr.edu/pub/carter/mech/saprc97>).

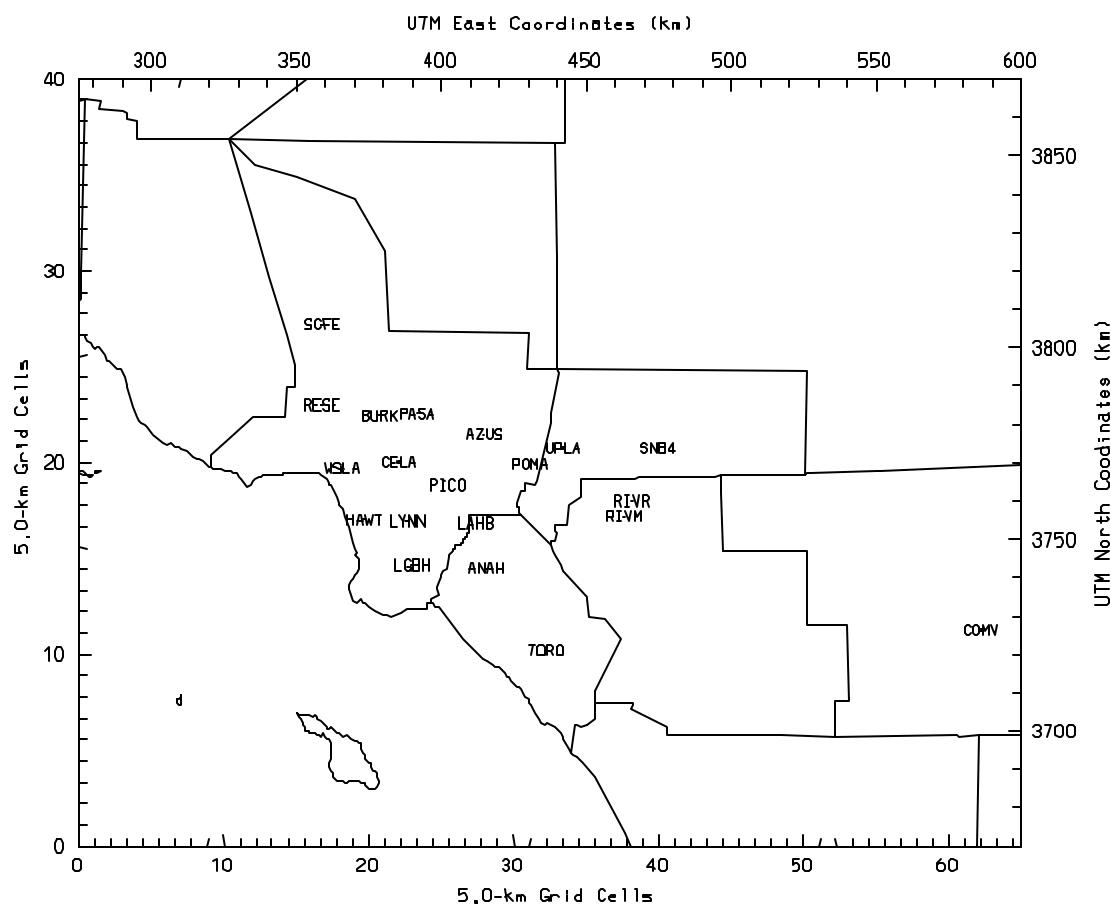
A complete listing of this photochemical mechanism is provided in the Attachment B-1. The list of hydrocarbon species that are treated explicitly is given in Table 2.1. Note that in the SAPRC97 chemical mechanism, PPN is used to lump peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates. Thus, modeled PPN cannot be compared directly with measured PPN. In addition to the species listed in Table 2.1, the photochemical mechanism includes a large number of species that are generated by the oxidation of hydrocarbons, as well as a set of chemical reactions that represents the inorganic reactions that take place in air. The mechanism used in our simulations has a total of 99 species and 204 reactions, of which 20 are photolytic. Of the 99 species, 29 are treated as steady state, 4 species are held constant, and hourly average concentrations are generated by the UAM-FCM for the other 66 species.

**Table 2.1 List of Hydrocarbon Species Treated Explicitly in SAPRC97**

Name	Symbol
<b>Formaldehyde (secondary)</b>	HCHO
<b>Formaldehyde (primary)</b>	FORM
<b>Acetaldehyde (secondary)</b>	CCHO
<b>Acetaldehyde (primary)</b>	ALD
<b>Acetone</b>	ACET
<b>Methyl ethyl ketone</b>	MEK
<b>Peroxyacetyl nitrate</b>	PAN
<b>Peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates</b>	PPN
<b>Methane</b>	CH4
<b>Ethene</b>	ETHE
<b>Isoprene</b>	ISOP
<b>Benzene</b>	C6H6
<b>1,3-Butadiene</b>	BUTD
<b>p-Dichlorobenzene</b>	PDCB
<b>Perchloroethylene</b>	PERC
<b>Dichloromethylene</b>	DICM
<b>Ethanol</b>	ETOH
<b>Methyl <i>tertiary</i>-butyl ether</b>	MTBE
<b>Glyoxal</b>	GLY
<b>Methyl Glyoxal</b>	MGLY
<b>Benzaldehyde</b>	BALD
<b>Cresols</b>	CRES
<b>Phenols</b>	PHEN

## B-2.4. Computer

The executable UAM-FCM files were prepared and compiled according to the recommended procedure by Kumar *et al.* (1995). The emission inventory corresponding to each year and case under study were used to calculate the reaction rates and product yields of the lumped species. All simulations were run on a Unix workstation. The time to run a 24-hour episode simulation was about 2 hours and twenty minutes.

**Figure 2.1 Modeling Domain**

## B-3. Model Input Description

### B-3.1. Episode and Domain

The UAM-FCM was applied to a three-day summer ozone episode in the South Coast, the August 26-28, 1987 Southern California Air Quality Study (SCAQS) episode (Lawson, 1990). The SCAQS domain has been gridded into 65 x 40 x 5 cells. Each horizontal square cell is 5 x 5 km<sup>2</sup>, with varying vertical height. The origin of the domain is at (275, 3670) in UTM coordinates (Zone 11). The domain is shown in Figure 2.1. It includes the counties of Los Angeles, Orange, and Kern, and portions of Riverside, San Diego, San Bernardino, and Ventura counties.

The August 26-28, 1987 SCAQS episode corresponds to an episode with very high observed ozone concentrations. We believe that the meteorological conditions of the episode represent close to worst-case conditions conducive to high pollutant concentrations. The SCAQS domain also contains a large fraction of the population in the State. Therefore, this episode and domain also represent worst-case conditions for exposure analysis of photochemically generated pollutants (e.g., ozone, NO<sub>2</sub>, acetaldehyde, formaldehyde, PAN and PPN). For these reasons we believe that modeling of this single episode is sufficient for our study. Worst-case conditions for directly emitted pollutants (e.g., CO, benzene, 1,3-butadiene, ethanol, and MTBE) are more readily inferred from air quality measurement (see Appendix C).

### B-3.2. Basic Input Files

The UAM-FCM requires 13 input files that provide information on the initial and boundary conditions of the domain, temperature, wind direction, wind speed, terrain, photolytic rates, reaction rate constants, and product yields, and emissions from area and point sources. Mobile sources and biogenic emissions are included in the area source file. The files used in our simulations, (except for the initial and boundary conditions, and area and point source emissions) were prepared by the South Coast Air Quality Management District for the 1994 State Implementation Plan (SCAQMD, 1994). The same diffusion break, region top, metscalars, terrain, temperature, and meteorological input files were used in all simulations, since these characterize the meteorological conditions for the episode and terrain. Table 3.1 provides a description of these files. Other files, such as initial and boundary conditions, point sources and area emissions were created for each specific simulation.

**Table 3.1 List of the Meteorological and Terrain Files for the SCAQS  
August 26-28, 1987 Episode**

Input File Identification	Description
ms238d11.b, ms239d11.b, ms240d11.b	Metscalar file
sim238bl, sim239bl, sim240bl	Control file
df238d11.b	Diffusion break file
tm238d11.b, tm239d11.b, tm240d11.b	Temperature file
rt238d11.b	Region top file
tr238d11.b	Terrain file
wd238d11.b, wd239d11.b, wd240d11.b	Wind file

### B-3.3. Region Top and Boundary Conditions

The region top and boundary conditions (together with the point and area sources) are specific to each of the different scenarios considered in this modeling study. The scenarios considered include the years 1997 and 2003 with different types of gasoline. These scenarios are listed in Table 3.2.

**Table 3.2 Scenarios Considered for the Photochemical Modeling**

Scenario	Description of Motor Vehicle Fuel Used
1997 MTBE	Current MTBE-based California Phase 2 Reformulated Gasoline (CaRFG)
2003 MTBE	Year 2003 MTBE-based CaRFG
2003 Et2.0%	Year 2003 Ethanol-based fully complying fuel (with oxygen content of 2.0 wt%)
2003 Et3.5%	Year 2003 Ethanol-based fully complying fuel (with oxygen content of 3.5 wt%)
2003 NonOxy	Year 2003 Non-oxygenated fully complying fuel

The region top and boundary condition files describe the air quality at the boundaries of the domain under study. These two files specify hourly ambient levels of each of the species in the SAPRC mechanism. For these simulations the region top and boundary conditions were treated as constant for all species throughout the episode. Region top concentrations were essentially the same as those used for the boundary conditions. Table 3.3 and Table 3.4 show the pollutant concentrations used for the boundary and region top, respectively.

**Table 3.3 Baseline Boundary Concentration (ppb)**

Species	1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
O3	40.0	40.0	40.0	40.0	40.0
NO	0.9095	0.8285	0.8285	0.8285	0.8285
NO2	1.6832	1.4	1.4	1.4	1.4
N2O5	1.0	1.0	1.0	1.0	1.0
HONO	0.08371	0.06913	0.06913	0.06913	0.06913
CO	200.0	200.0	200.0	200.0	200.0
CO2	1000.0	1000.0	1000.0	1000.0	1000.0
CCHO	0.5	0.53	0.53	0.53	0.53
HCHO	0.5	0.5	0.5	0.5	0.5
RCHO	0.98	0.98	0.98	0.98	0.98
ETHE	0.829	0.7626	0.7626	0.7626	0.7626
CH4	1720.0	1720.0	1720.0	1720.0	1720.0
ALK1	0.49	0.49	0.49	0.49	0.49
ALK2	1.01	1.01	1.01	1.01	1.01
ARO1	0.4273	0.3962	0.3962	0.3962	0.3962
ARO2	0.14507	0.13538	0.13538	0.13538	0.13538
OLE1	0.7048	0.69056	0.69056	0.69056	0.69056
OLE2	0.01	0.01	0.01	0.01	0.01
C6H6	0.08	0.08	0.08	0.08	0.08
NO3	1.0	1.0	1.0	1.0	1.0
HO2	0.1	0.1	0.1	0.1	0.1
MTBE	0.1	0.1	0.01	0.01	0.01
ETOH	0.01	0.01	0.3	0.41	0.01
All other species	0.01	0.01	0.01	0.01	0.01

**Table 3.4 Region Top Concentrations (ppb)**

Species	1997 MTBE	2003 MTBE	2003 Et2.0%	2003 Et3.5%	2003 NonOxy
O3	<b>40.0</b>	<b>40.0</b>	<b>40.0</b>	<b>40.0</b>	<b>40.0</b>
NO	<b>0.9095</b>	<b>0.8285</b>	<b>0.8285</b>	<b>0.8285</b>	<b>0.8285</b>
NO2	<b>1.6832</b>	<b>1.4</b>	<b>1.4</b>	<b>1.4</b>	<b>1.4</b>
N2O5	<b>1.0</b>	<b>1.0</b>	<b>1.0</b>	<b>1.0</b>	<b>1.0</b>
HONO	<b>0.08371</b>	<b>0.06913</b>	<b>0.06913</b>	<b>0.06913</b>	<b>0.06913</b>
CO	<b>200.0</b>	<b>200.0</b>	<b>200.0</b>	<b>200.0</b>	<b>200.0</b>
CO2	<b>1000.0</b>	<b>1000.0</b>	<b>1000.0</b>	<b>1000.0</b>	<b>1000.0</b>
CCHO	<b>0.5</b>	<b>0.53</b>	<b>0.53</b>	<b>0.53</b>	<b>0.53</b>
HCHO	<b>0.5</b>	<b>0.5</b>	<b>0.5</b>	<b>0.5</b>	<b>0.5</b>
RCHO	<b>0.98</b>	<b>0.98</b>	<b>0.98</b>	<b>0.98</b>	<b>0.98</b>
ETHE	<b>0.829</b>	<b>0.7626</b>	<b>0.7626</b>	<b>0.7626</b>	<b>0.7626</b>
CH4	<b>1720.0</b>	<b>1720.0</b>	<b>1720.0</b>	<b>1720.0</b>	<b>1720.0</b>
ALK1	<b>0.49</b>	<b>0.49</b>	<b>0.49</b>	<b>0.49</b>	<b>0.49</b>
ALK2	<b>1.0</b>	<b>1.0</b>	<b>1.0</b>	<b>1.0</b>	<b>1.0</b>
ARO1	<b>0.4218</b>	<b>0.3912</b>	<b>0.3912</b>	<b>0.3912</b>	<b>0.3912</b>
ARO2	<b>0.14507</b>	<b>0.13538</b>	<b>0.13538</b>	<b>0.13538</b>	<b>0.13538</b>
OLE1	<b>0.7048</b>	<b>0.69056</b>	<b>0.69056</b>	<b>0.69056</b>	<b>0.69056</b>
OLE2	<b>0.01</b>	<b>0.01</b>	<b>0.01</b>	<b>0.01</b>	<b>0.01</b>
C6H6	<b>0.08</b>	<b>0.08</b>	<b>0.08</b>	<b>0.08</b>	<b>0.08</b>
NO3	<b>1.0</b>	<b>1.0</b>	<b>1.0</b>	<b>1.0</b>	<b>1.0</b>
HO2	<b>0.1</b>	<b>0.1</b>	<b>0.1</b>	<b>0.1</b>	<b>0.1</b>
MTBE	<b>0.1</b>	<b>0.1</b>	<b>0.01</b>	<b>0.01</b>	<b>0.01</b>
ETOH	<b>0.01</b>	<b>0.01</b>	<b>0.3</b>	<b>0.41</b>	<b>0.01</b>
All other species	<b>0.01</b>	<b>0.01</b>	<b>0.01</b>	<b>0.01</b>	<b>0.01</b>

### B-3.4. Initial Conditions

All simulations were started with the same initial conditions given in Table 3.5. Because of this, only the results of the last simulation day, August 28, are used in the analysis. The results of the last simulation day, based on our past experience, are insensitive to the initial conditions.

**Table 3.5 Initial Species Concentrations (ppb)**

Species	Concentration
O3	70.0
NO	1.0
NO2	2.0
HNO3	0.1
HONO	0.1
CO	200.0
CO2	0.1
H2O2	0.1
CCHO	1.1
HCHO	5.8
RCHO	0.98
ETHE	1.4
CH4	1720.0
ALK1	0.49
ALK2	1.01
ARO1	0.7
ARO2	0.23
OLE1	0.83
OLE2	0.23
OLE3	0.00
C6H6	0.16
All other species	0.01

### B-3.5. Point and Area Sources

Point source emission and area source emission files were prepared for each specific scenario studied. The preparation of each file is discussed in Appendix A.

### B-3.6. Air Quality Monitoring Sites

Table 3.6 lists the 20 air quality monitoring sites in the South Coast modeling domain used to analyze the results of each different scenario studied. In addition to these sites, the domain maximum was also used. Table 3.6 shows the site locations in the domain.

**Table 3.6 Sites in the Modeling Domain Used to Study the Impact of Each of the Scenarios Studied**

Site Name	Id
Anaheim	ANAH
Azusa	AZUS
Burbank	BURK
Los Angeles North Main	CELA
Costa Mesa - Mesa Verde Drive	COMV
Hawthorne	HAWT
La Habra	LABH
North Long Beach	LGBH
Lynwood	LYNN
Pasadena - S. Wilson Avenue	PASA
Pico Rivera	PICO
Pomona	POMA
Reseda	RESE
Riverside - Rubidoux	RIVR
Riverside - Magnolia	RIVM
Santa Clarita - County Fire Station	SCFE
San Bernardino - 4 <sup>th</sup> Street	SNB4
El Toro	TORO
Upland	UPLA
West Los Angeles - VA Hospital	WSLA

## B-4. Results

As indicated above, only the results of the third day of the episode simulated (August 28) were used in the analysis to avoid dependence on the initial conditions.

### B-4.1. Domain Maximum 1-Hour-Average Concentrations

Table 4.1 shows the domain maximum concentration of the pollutants of interest for each scenario simulated. As shown in Table 4.1, the domain maximum ozone decreases (6 - 8%) from 1997 to 2003 because of reductions in overall emissions. CO shows a more significant decrease (25 - 35%). Nitric acid and ethanol both decrease by up to 9%. It appears that the maximum 1-hour-average ethanol concentration is dominated by non-motor vehicle emission sources. Although domain ethanol emissions have increased

from 1997 to 2003, reflecting changes to the motor vehicle cleaner burning gasoline used, the emissions from non-motor vehicle sources (which appear to dominate the magnitude of the maximum ethanol concentration) have decreased. In general the predicted concentrations do not show a large change from 1997 to 2003 for most of the pollutants, except for NO, NO<sub>2</sub>, CO, benzene, ethanol, and nitric acid.

Maximum ozone concentrations among the year 2003 simulations are very similar, within 1-2%. CO concentration is higher for the NonOxy scenario among the 2003 simulations, and is lowest for the Et3.5% scenario.

**Table 4.1 Domain Maximum 1-Hour-Average Concentrations for Each Scenario**

Simulation	Domain Maximum 1-Hour-Average Concentration (ppb)												
	O <sub>3</sub>	NO	NO <sub>2</sub>	CO	Formaldehyde	Acetaldehyde	C <sub>6</sub> H <sub>6</sub>	BUTD	MTBE	ETOH	PAN	PPN	HNO <sub>3</sub>
1997 MTBE	235.9	214.3	105.3	3,023.6	22.7	9.2	3.4	3.0	6.1	45.6	4.4	1.4	57.7
2003 MTBE	222.2	190.7	97.2	2,189.1	23.0	8.7	1.9	3.0	3.9	41.4	4.2	1.4	52.3
2003 Et2.0%	220.2	190.6	97.0	2,189.1	22.7	8.8	1.9	3.0	0.0	42.3	4.1	1.4	52.3
2003 Et3.5%	220.1	190.6	97.1	1,968.1	22.9	8.9	2.0	3.0	0.0	42.8	4.2	1.4	52.2
2003 NonOxy	220.4	190.6	97.0	2,262.6	22.7	8.8	1.9	3.0	0.0	41.4	4.0	1.4	52.4

<sup>a</sup> Formaldehyde and acetaldehyde refer to total concentrations from primary emissions and secondary formation, C<sub>6</sub>H<sub>6</sub> is benzene, BUTD is 1,3 -butadiene, MTBE is methyl *tertiary*-butyl ether, ETOH is ethanol, PAN is peroxyacetyl nitrate, PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates, and HNO<sub>3</sub> is nitric acid.

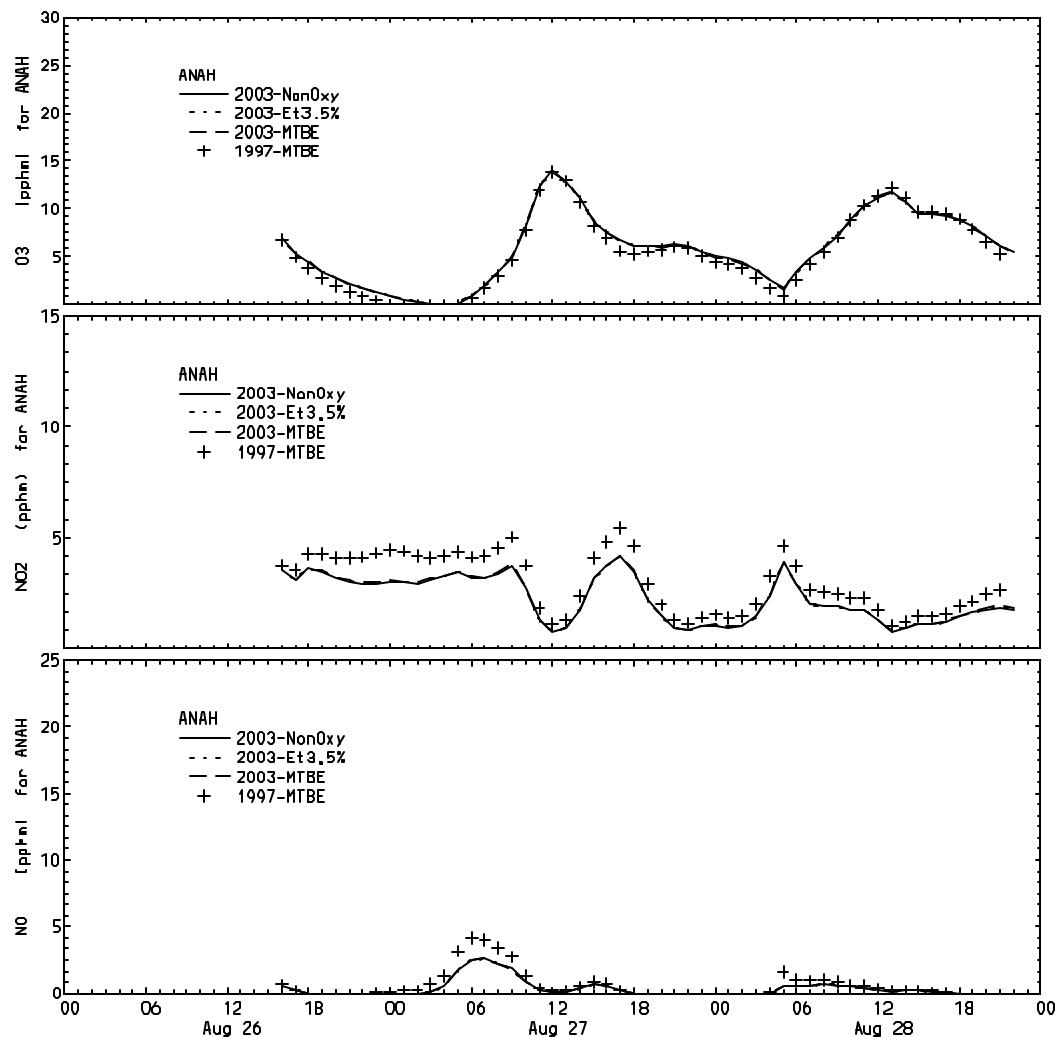
Figure 4.1 through Figure 4.5 show hourly ozone, NO, and NO<sub>2</sub> for August 26-28, 1987 at Anaheim (ANAH), Burbank (BURK), downtown Los Angeles (CELA), Riverside-Rubidoux (RIVR), and at the grid cell with the domain maximum (GMX). The time plots clearly show that the 1997 and 2003 scenarios have very similar predicted ozone concentrations during the last day of the simulation. There are significant differences in predicted NO<sub>2</sub> concentrations between 1997 and 2003, as expected. All 2003 scenarios have the essentially the same predicted NO and NO<sub>2</sub> hourly concentrations.

Figure 4.6 through Figure 4.10 show ethanol, MTBE, and CO time series plots for August 26-28, 1987 at Anaheim, Burbank, downtown Los Angeles, Riverside-Rubidoux, and at the grid with the domain maximum. The plots are only for the 2003 scenarios (Et2.0%, Et3.5%, NonOxy, and MTBE). As expected, the 2003 Et3.5% scenario has highest predicted ethanol concentrations, while the 2003 MTBE is the only scenario with significant MTBE hourly concentrations among all the 2003 scenarios.

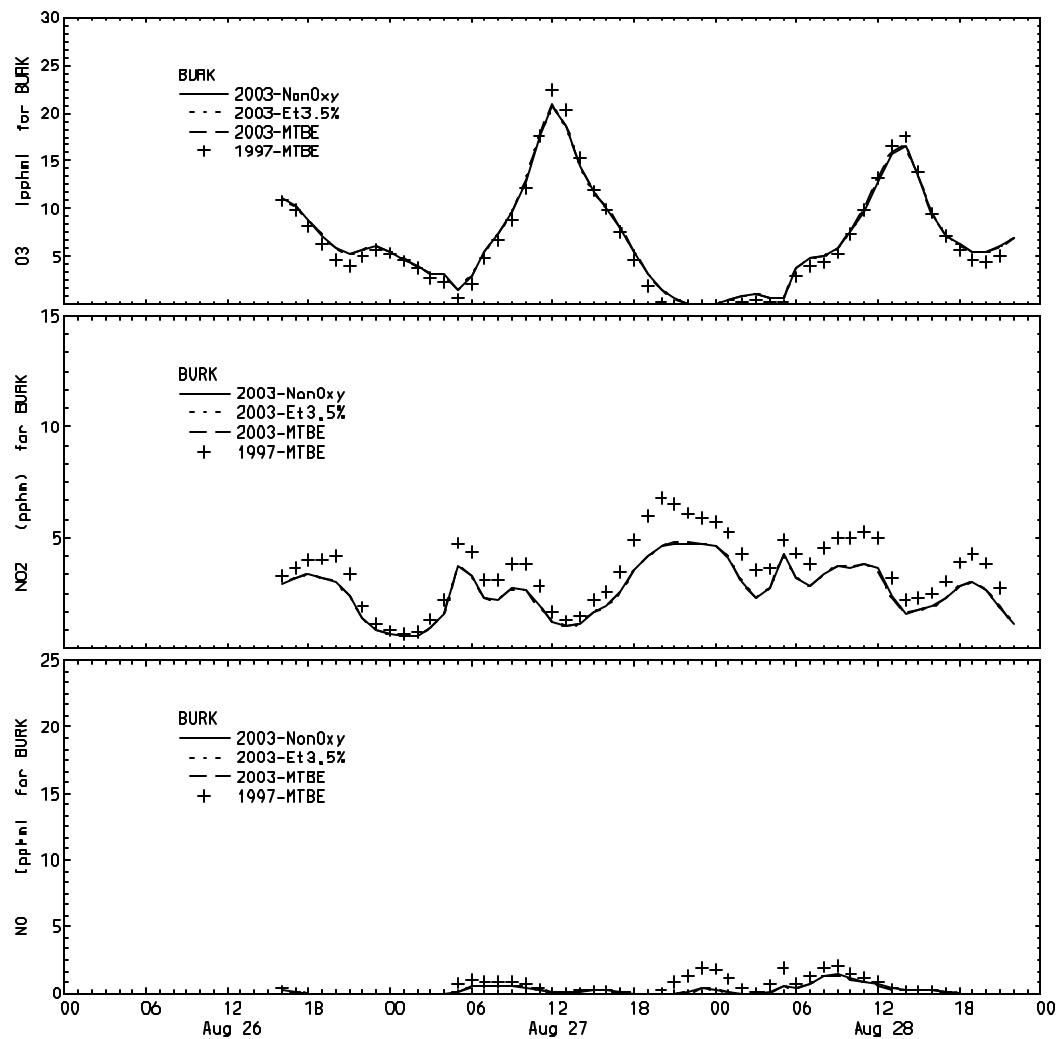
Figure 4.11 through Figure 4.15 show time series plots of hourly PAN (and higher molecular weight acyl peroxy nitrates), and nitric acid concentrations for August 26-28, 1987 at Anaheim, Burbank, downtown Los Angeles, Riverside-Rubidoux, and at the domain maximum. Predicted PAN, PPN, and nitric acid concentrations are the

same for all 2003 scenarios. Both PAN and PPN show a large maximum on the second day of the episode that has significantly decreased by the third day of the episode simulated.

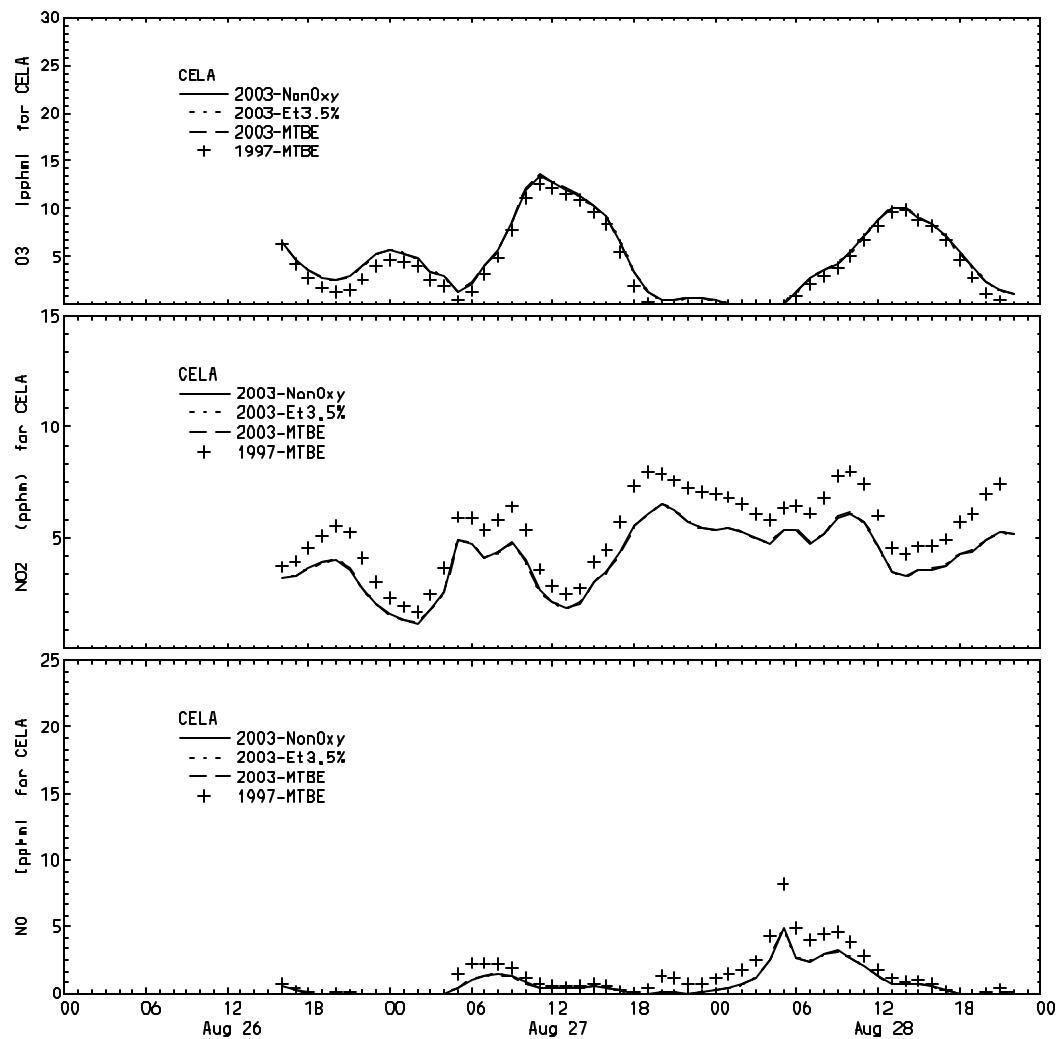
From Figure 4.1 through Figure 4.5, it is clear that although hydrocarbon and NO<sub>x</sub> emissions decreased from 1997 to 2003, the reduction did not significantly impact the radical flux levels predicted by the photochemical mechanism. This is confirmed by the small impact on the predicted maximum ozone concentrations. In addition, the NO<sub>x</sub>-to-hydrocarbon ratio may not have significantly changed from 1997 to 2003, which may explain the essentially similar PAN, PPN (and higher molecular weight acyl peroxy nitrates), and nitric acid predicted concentrations for these years (see Figure 4.11 through Figure 4.15).



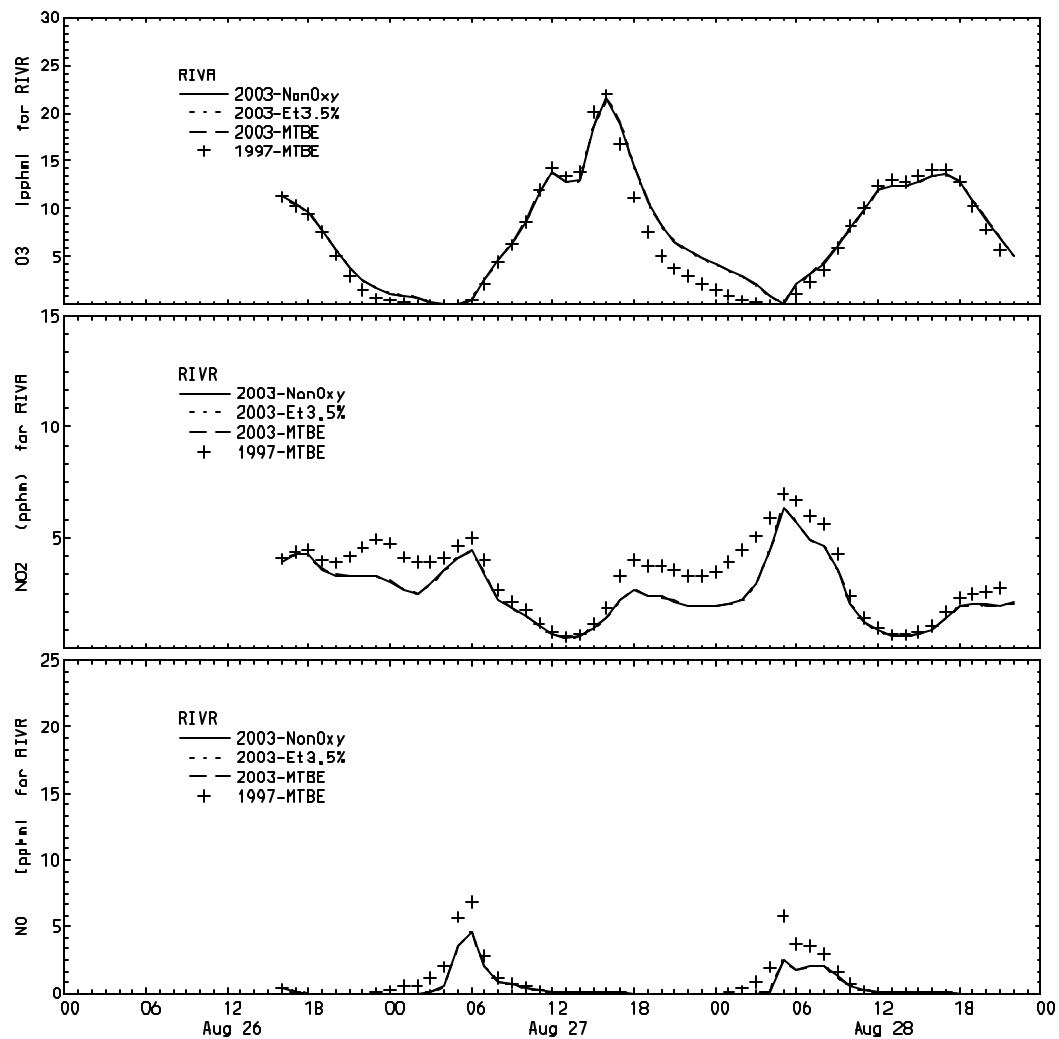
**Figure 4.1 Time Series for Ozone, NO<sub>2</sub>, and NO at Anaheim for 1997 and 2003 Scenarios**



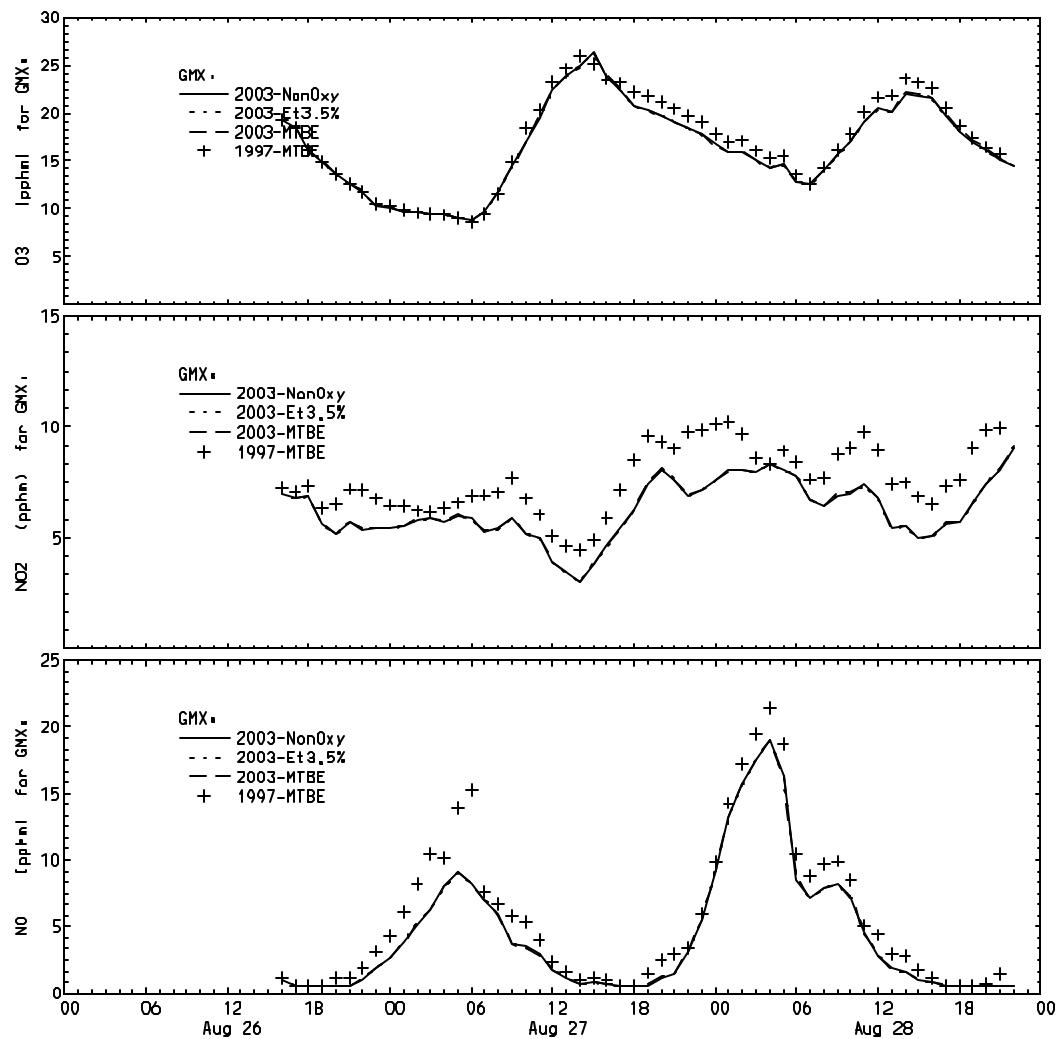
**Figure 4.2 Time Series for Ozone, NO<sub>2</sub>, and NO at Burbank for 1997 and 2003 Scenarios**



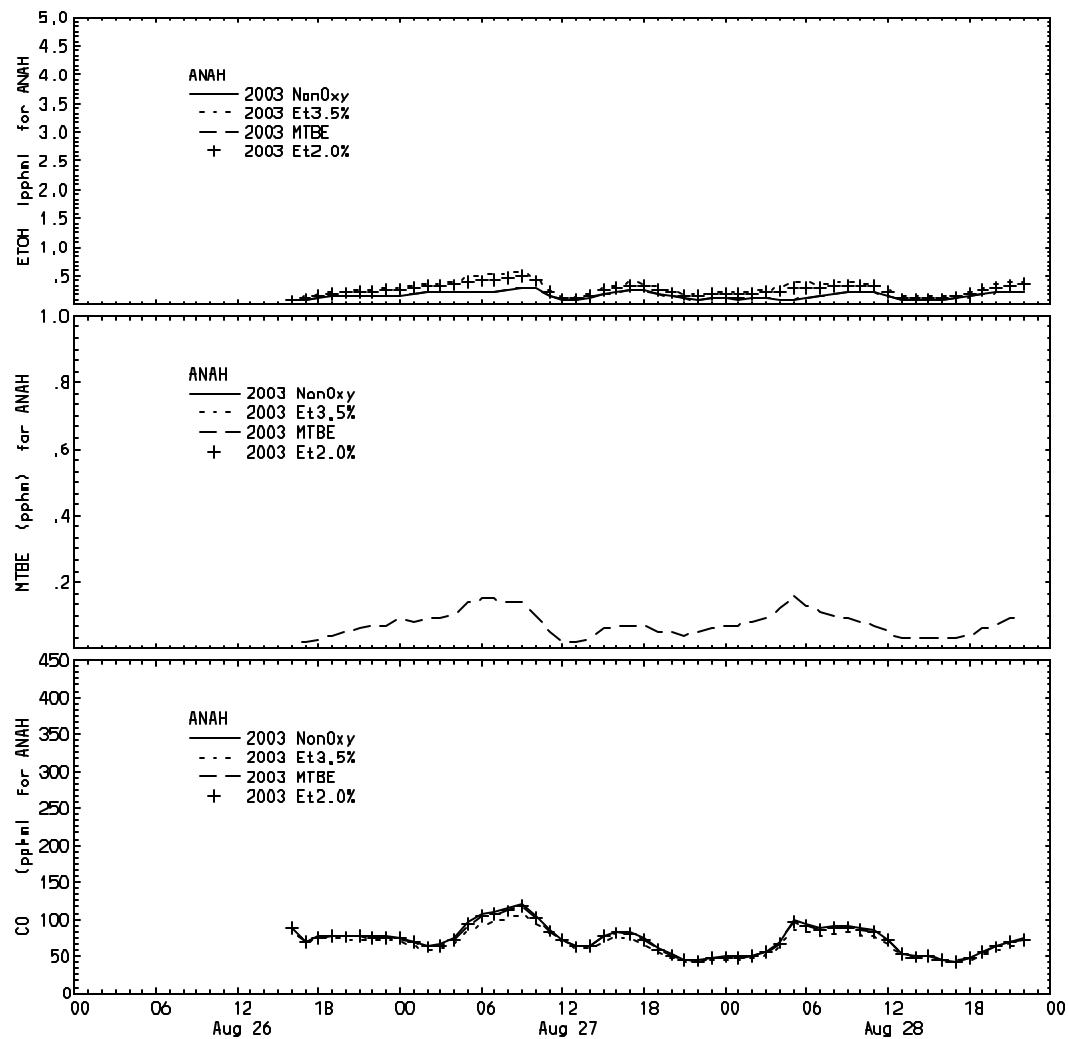
**Figure 4.3 Time Series for Ozone, NO<sub>2</sub>, and NO at Los Angeles for 1997 and 2003 Scenarios**



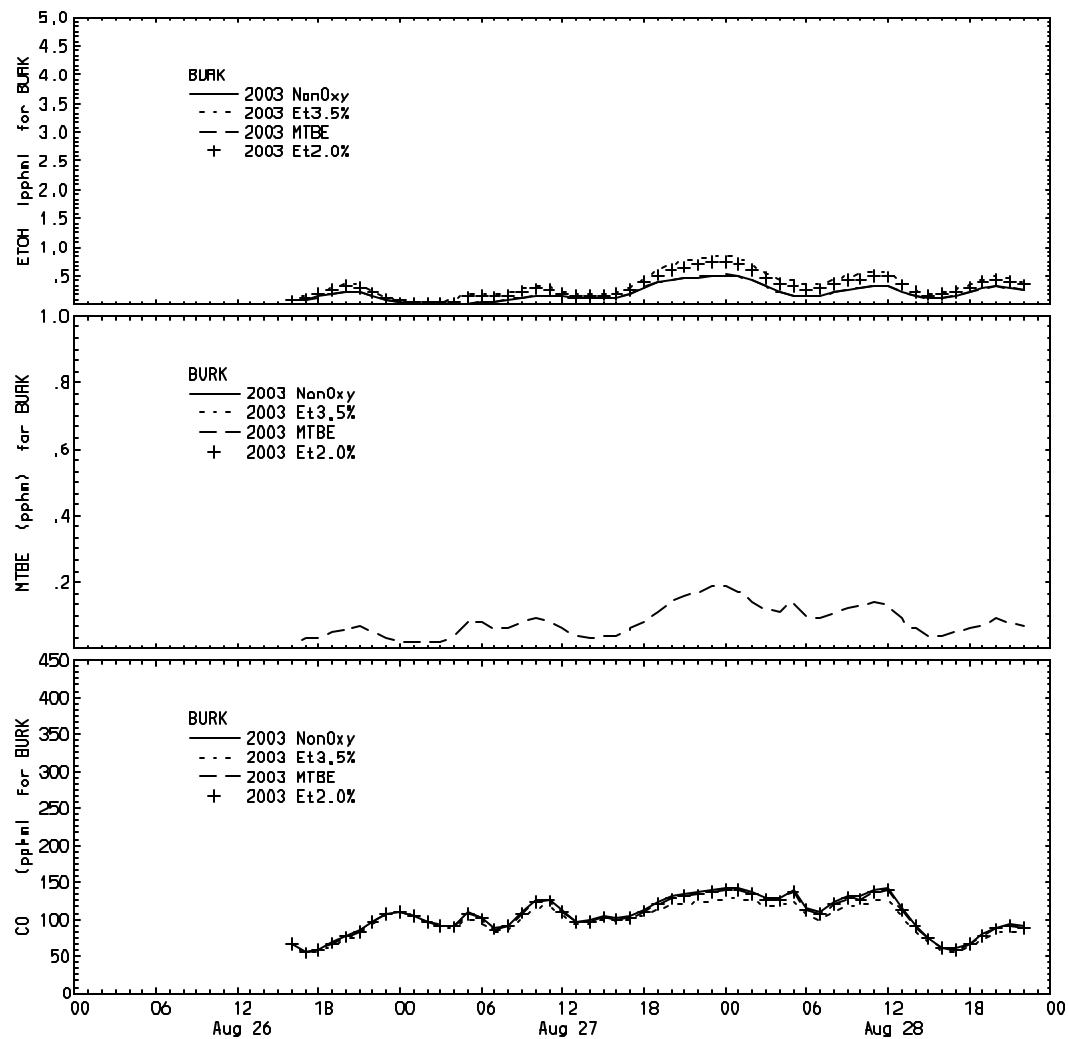
**Figure 4.4 Time Series for Ozone, NO<sub>2</sub>, and NO at Riverside for 1997 and 2003 Scenarios**



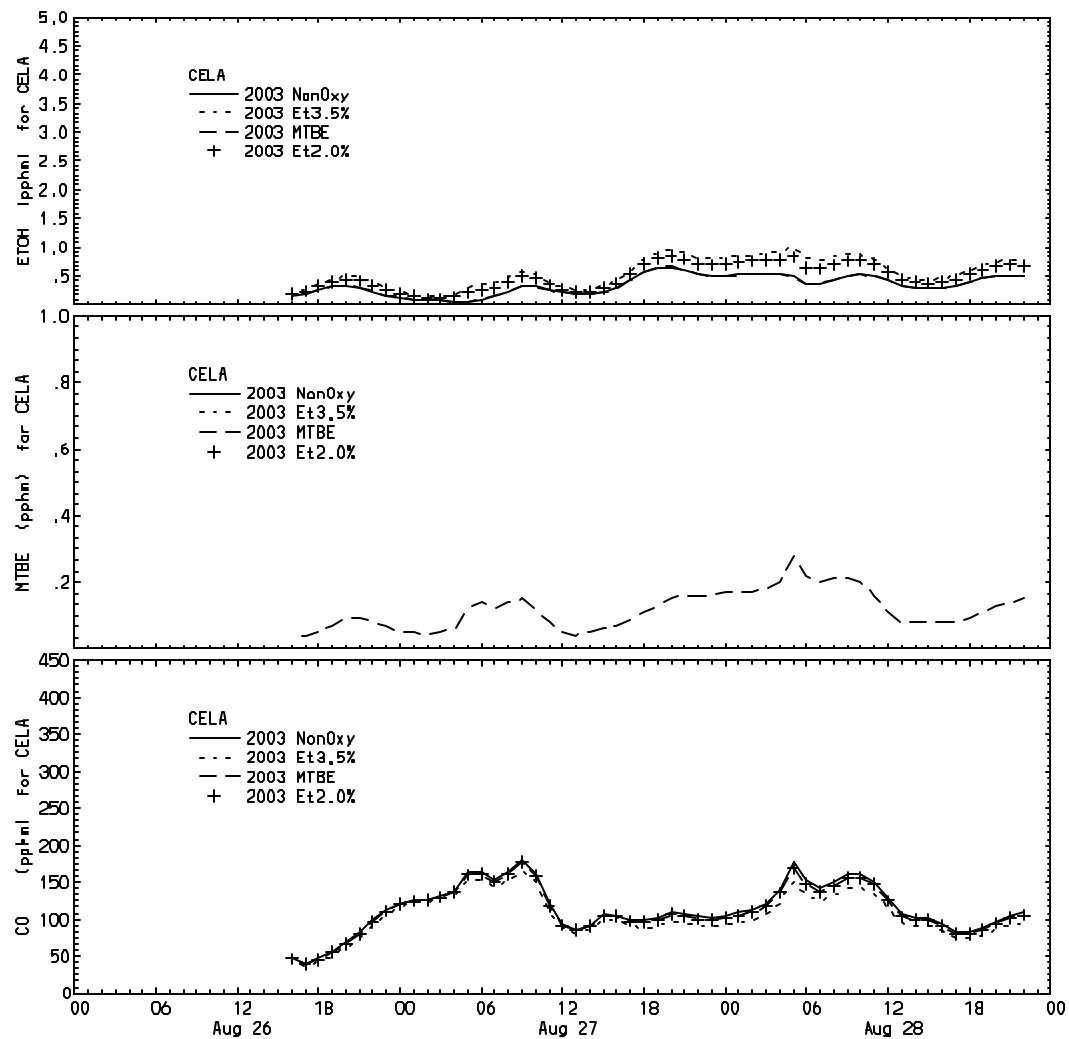
**Figure 4.5 Time Series for Ozone, NO<sub>2</sub>, and NO at Grid with Domain Maximum for 1997 and 2003 Scenarios**



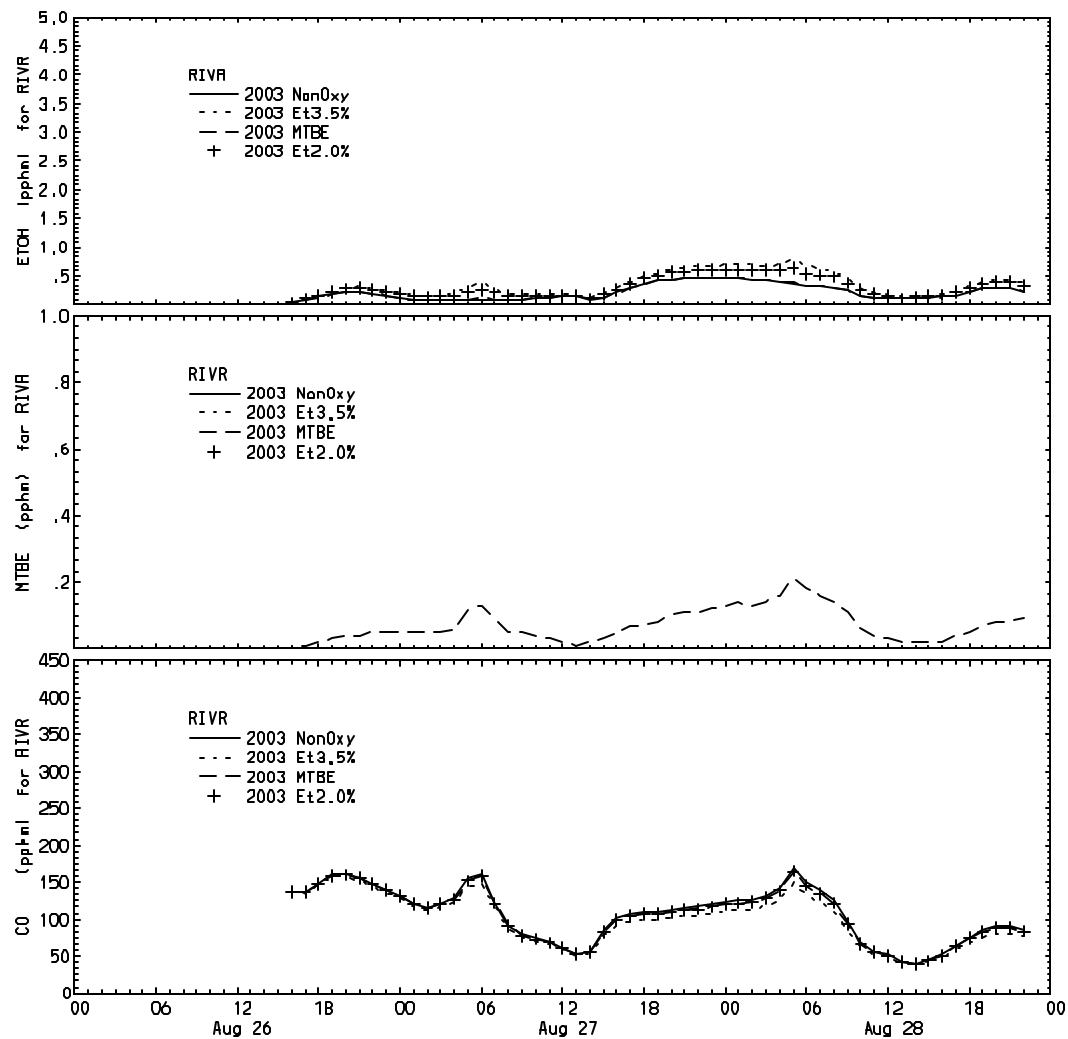
**Figure 4.6 Time Series for MTBE, Ethanol, and CO at Anaheim for 2003 Scenarios**



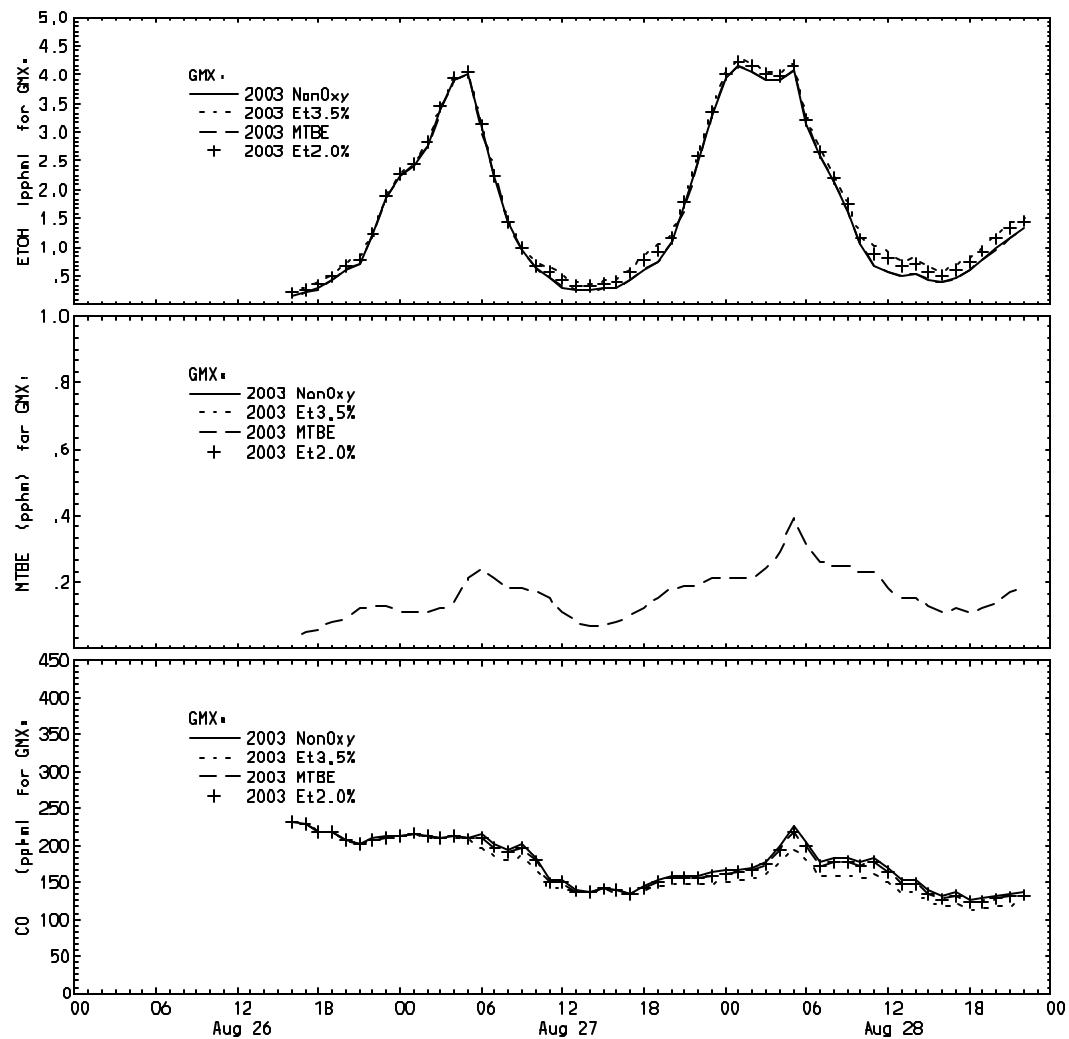
**Figure 4.7 Time Series for MTBE, Ethanol, and CO at Burbank for 2003 Scenarios**



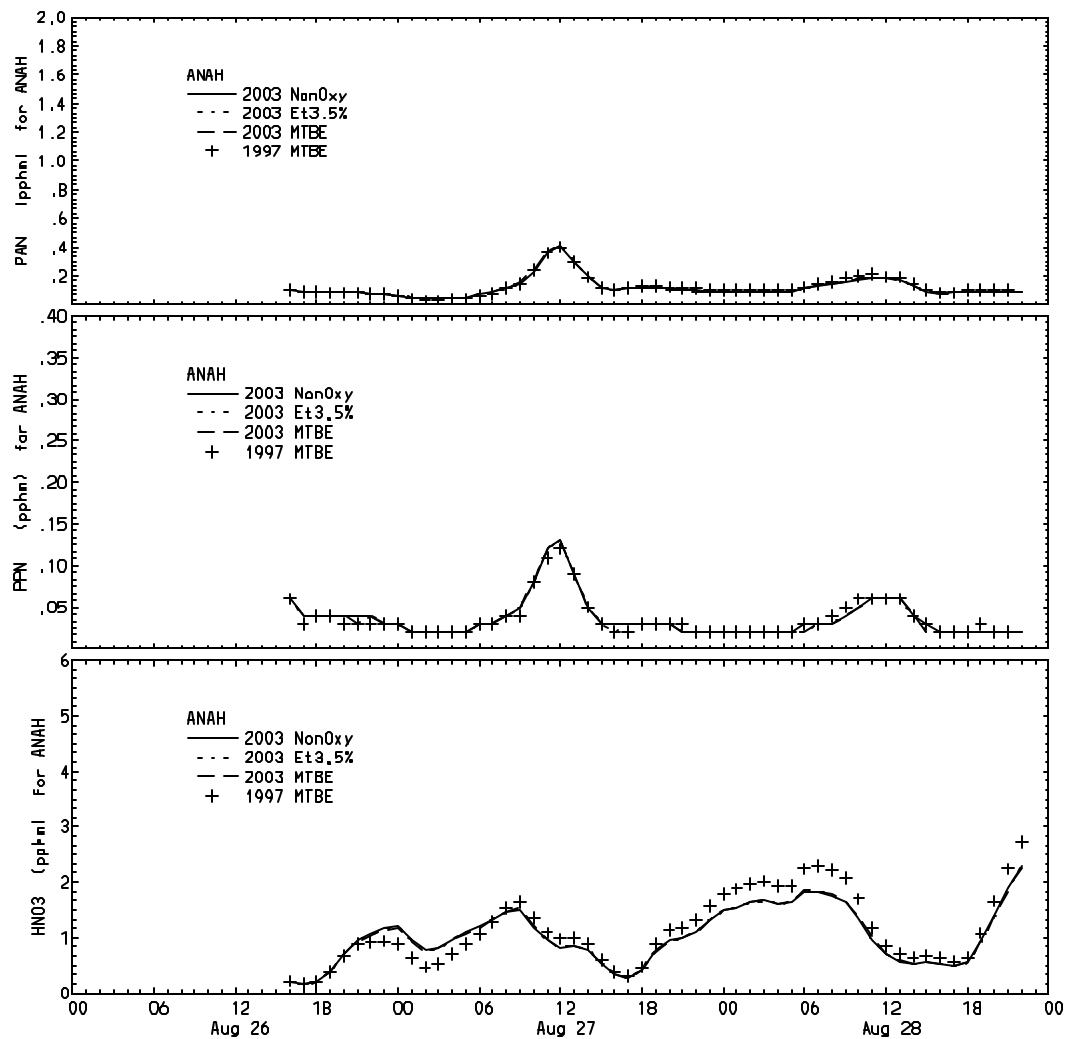
**Figure 4.8 Time Series for MTBE, Ethanol, and CO at Los Angeles for 2003 Scenarios**



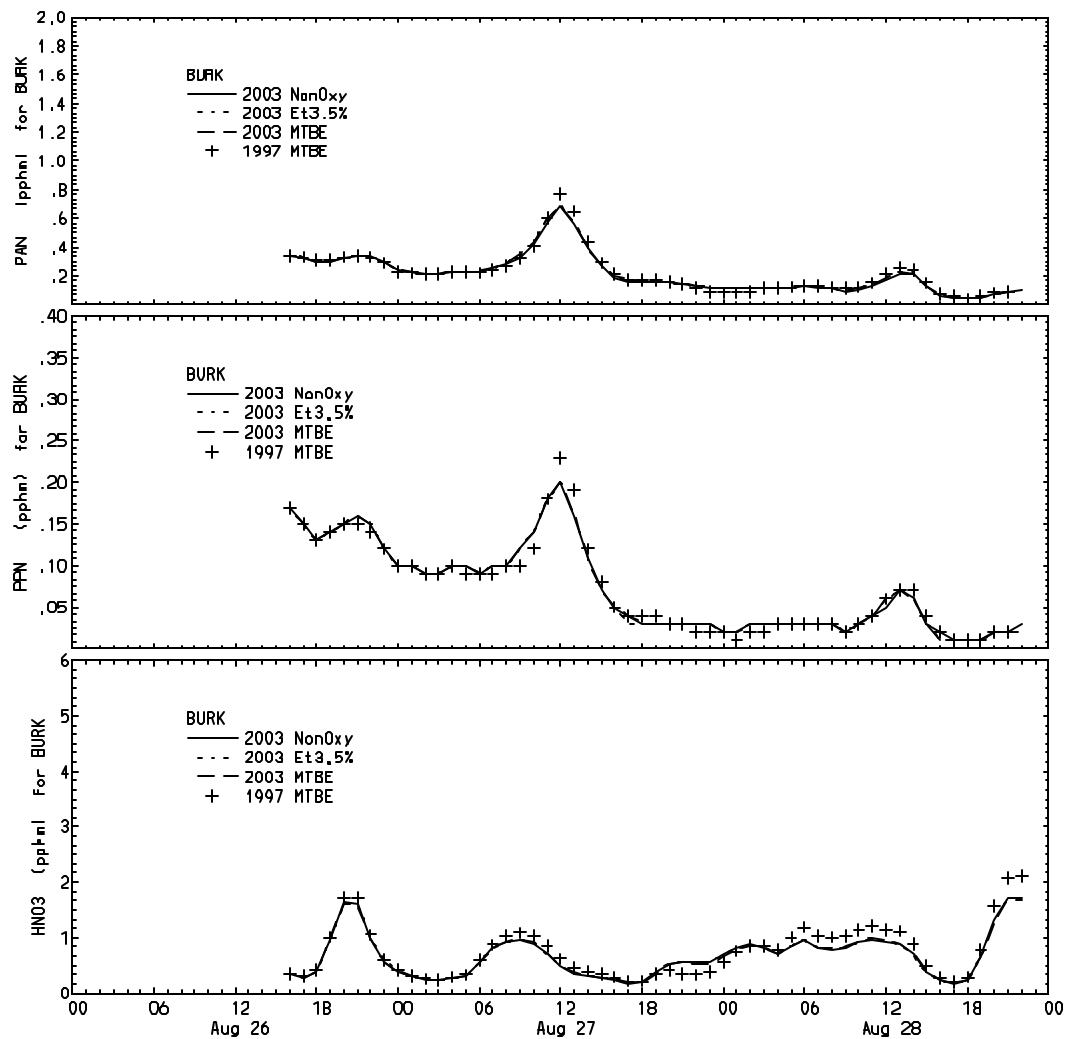
**Figure 4.9 Time Series for MTBE, Ethanol, and CO at Riverside for 2003 Scenarios**



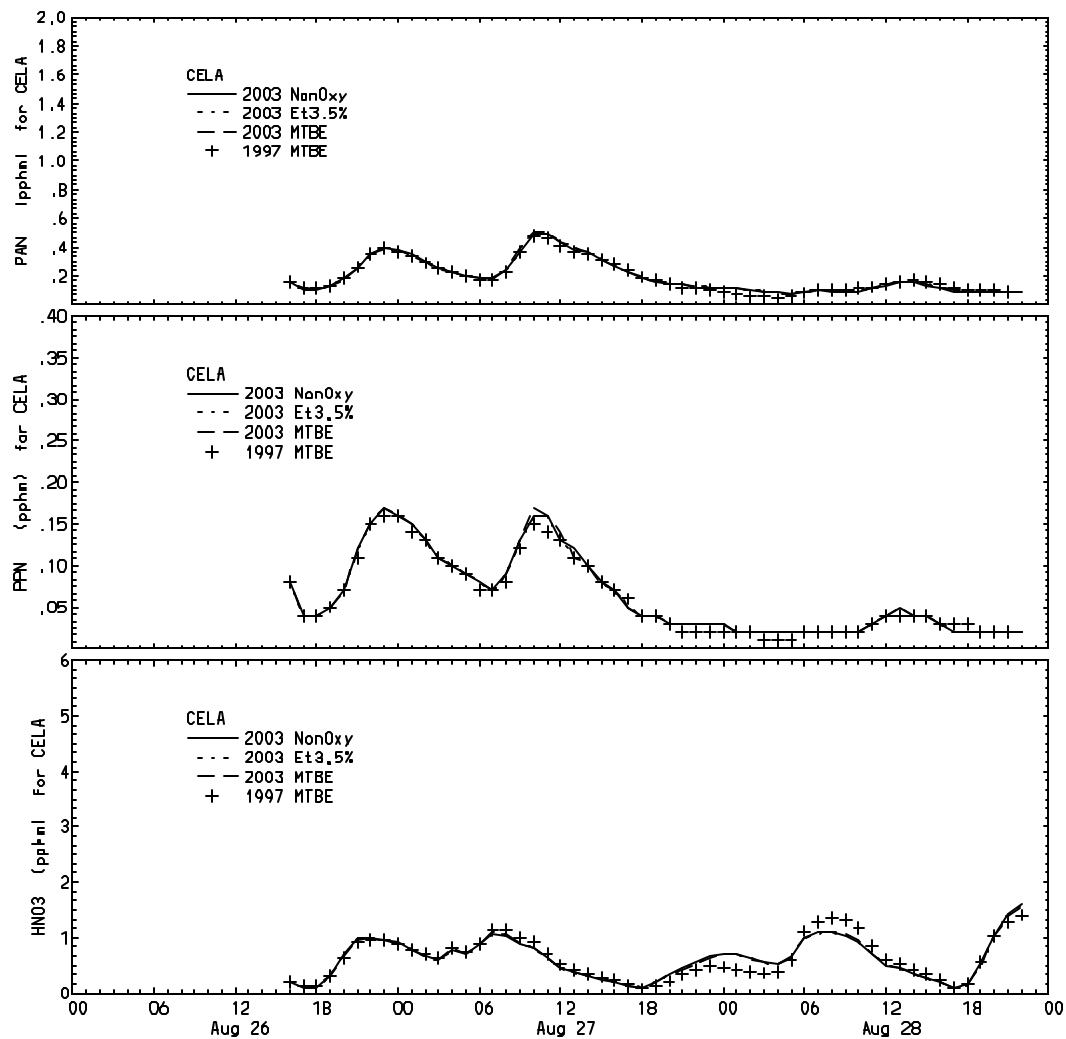
**Figure 4.10 Time Series for MTBE, Ethanol, and CO at Grid with Domain Maximum for 2003 Scenarios**



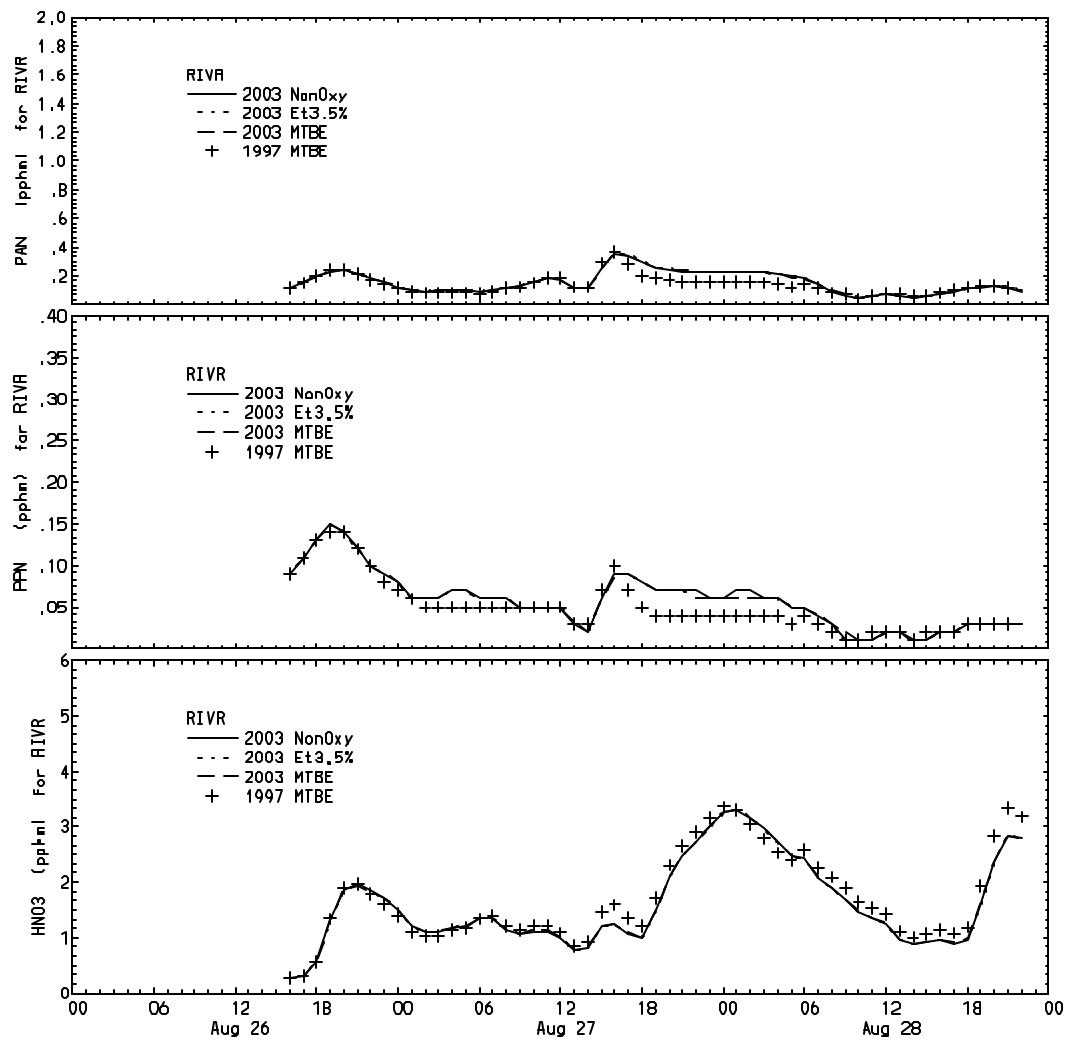
**Figure 4.11 Time Series for PAN, PPN, and Nitric Acid at Anaheim for 1997 and 2003 Scenarios**



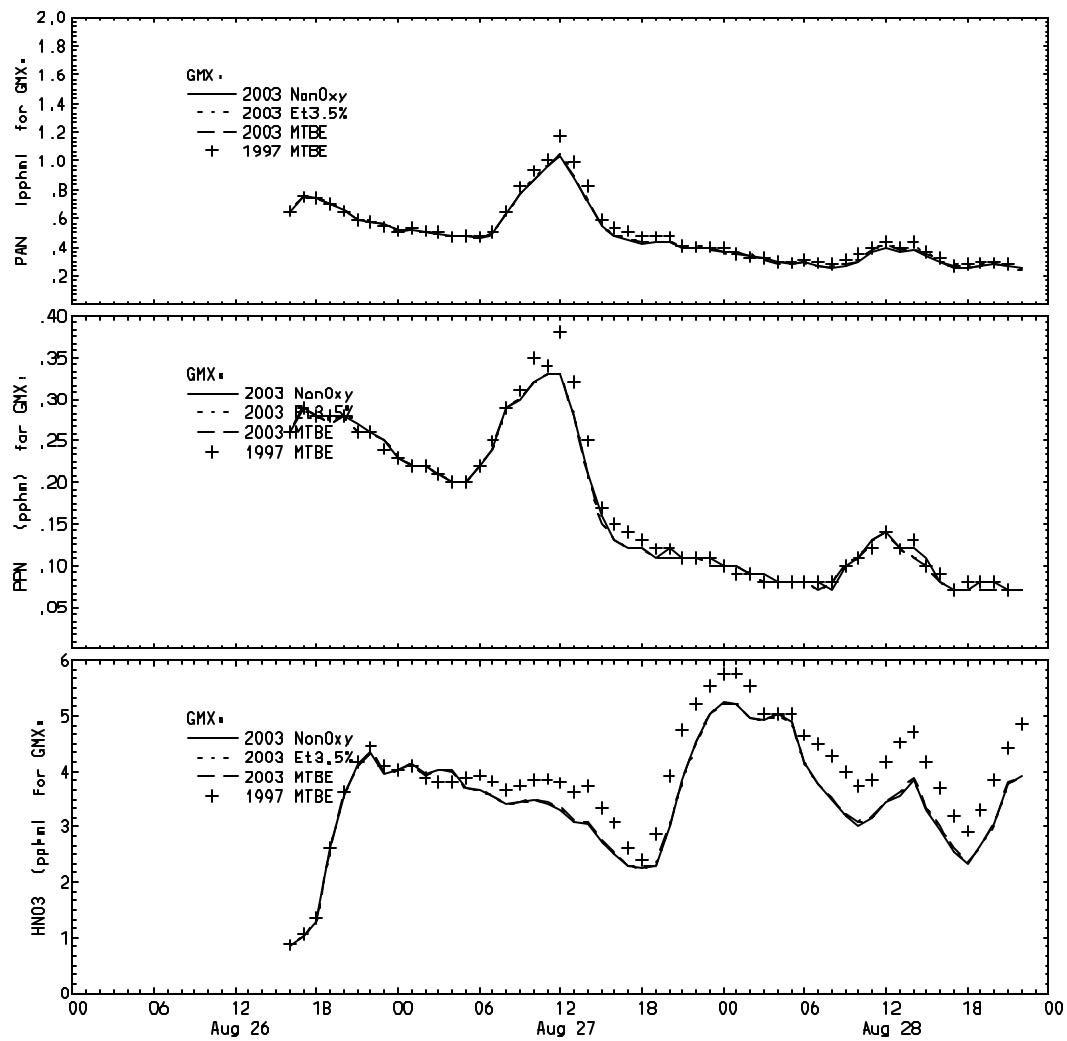
**Figure 4.12 Time Series for PAN, PPN, and Nitric Acid at Burbank for 1997 and 2003 Scenarios**



**Figure 4.13 Time Series for PAN, PPN, and Nitric Acid at Los Angeles for 1997 and 2003 Scenarios**



**Figure 4.14 Time Series for PAN, PPN, and Nitric Acid at Riverside for 1997 and 2003 Scenarios**



**Figure 4.15 Time Series for PAN, PPN, and Nitric Acid at Grid with Domain Maximum for 1997 and 2003 Scenarios**

## B-4.2. Domain Maximum 8-Hour-Average Concentrations

Table 4.2 shows domain maximum 8-hour-average concentrations for selected pollutants. As shown, the 8-hour-average ozone concentration decreases by up to 5% from 1997 to 2003. CO is reduced by up to 32% for the Et3.5% scenario. Similarly, the 8-hour benzene concentration is reduced by 37% between 1997 and 2003. The 8-hour-average formaldehyde is reduced by 4%, but the 8-hour-average acetaldehyde decreases by up to 13% from 1997. The 8-hour nitric acid predicted concentration is seen to decrease by 5% from 1997 to 2003, while 8hour PPN and BUTD are essentially unchanged. PAN and ethanol 8-hour-average concentrations decrease by up to 9% from 1997 baseline. As discussed in Section B-4.1, the predicted ethanol 24-hour concentration also appears to be dominated by non-motor vehicle sources, which may explain the predicted decrease in ethanol 8-hour-average concentrations

**Table 4.2 Domain Maximum 8-Hour-Average Concentrations for Each Scenario**

Simulation	Domain Maximum 8 -Hour-Average Concentration <sup>a</sup> (ppb)												
	O <sub>3</sub>	NO	NO <sub>2</sub>	CO	Formaldehyde	Acetaldehyde	C <sub>6</sub> H <sub>6</sub>	BUTD	MTBE	ETOH	PAN	PPN	HNO <sub>3</sub>
1997 MTBE	187.3	150.3	86.4	2,432	16.8	7.7	2.46	2.08	4.1	40.9	3.25	0.99	47.9
2003 MTBE	177.9	133.4	75.0	1,816	16.3	6.7	1.60	2.05	2.7	37.2	2.98	0.94	45.6
2003 Et2.0%	178.0	133.2	74.9	1,816	16.1	6.8	1.59	2.05	0.0	38.0	2.98	0.94	45.5
2003 Et3.5%	177.5	133.2	74.9	1,658	16.2	6.8	1.61	2.05	0.0	38.5	3.03	0.94	45.4
2003 NonOxy	178.3	133.2	75.0	1,872	16.1	6.8	1.56	2.05	0.0	37.2	2.96	0.95	45.6

<sup>a</sup> Formaldehyde and acetaldehyde refer to total concentrations from primary emissions and secondary formation, C<sub>6</sub>H<sub>6</sub> is benzene, BUTD is 1,3-butadiene, MTBE is methyl tertiary-butyl ether, ETOH is ethanol, PAN is peroxyacetyl nitrate, PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates, and HNO<sub>3</sub> is nitric acid.

## B-4.3. Domain Maximum 24-Hour-Average Concentrations

Table 4.3 shows maximum 24-hour-average concentrations in the domain for selected pollutants. As shown, the 24-hour-average ozone concentration decreases by up to 4% from 1997 to 2003. CO is reduced by up to 29% for the 2003 Et3.5% scenario. Similarly, the 24-hour benzene concentration is reduced by almost 37% between 1997 and 2003. The 24-hour-average formaldehyde is reduced by up to 16%, but the 24-hour-average acetaldehyde is unchanged. The 24-hour nitric acid concentration is seen to decrease by 12% from 1997 to 2003, while PPN decreases by 2% for the 2003 3.5%, increases by 3% for the 2003 NonOxy, and is unchanged for the 2003 MTBE and 2003 Et2.0%. The impact on 24-hour PAN concentration is also modest, with a decrease of up to 6% for the 2003 NonOxy scenario. The 24-hour-average ethanol concentration is reduced up to 9% for the 2003 NonOxy case. As discussed in Section B-4.1, the

predicted ethanol 24-hour concentration also appears to be dominated by non-motor vehicle sources, which may explain the predicted decrease in ethanol 8-hour-average concentrations.

**Table 4.3 Domain Maximum 24-Hour-Average Concentrations For Each Scenario**

Simulation	Domain Maximum 24-Hour-Average Concentration <sup>a</sup> (ppb)												
	O <sub>3</sub>	NO	NO <sub>2</sub>	CO	Formaldehyde	Acetaldehyde	C <sub>6</sub> H <sub>6</sub>	BUTD	MTBE	ETOH	PAN	PPN	HNO <sub>3</sub>
1997 MTBE	148.0	66.2	72.8	1,614	11.35	6.2	1.72	0.88	2.63	19.05	2.12	0.58	36.73
2003 MTBE	142.7	57.8	60.7	1,252	9.90	6.2	1.10	0.88	1.67	17.35	2.03	0.58	32.41
2003 Et2.0%	142.7	57.7	60.4	1,252	9.57	6.2	1.09	0.87	0.00	17.89	2.02	0.58	32.28
2003 Et3.5%	142.4	57.7	60.5	1,149	9.79	6.2	1.10	0.88	0.00	18.14	2.06	0.57	32.24
2003 NonOxy	142.9	57.7	60.5	1,286	9.49	6.2	1.06	0.87	0.00	17.36	2.00	0.60	32.28

<sup>a</sup> Formaldehyde and acetaldehyde refer to total concentrations from primary emissions and secondary formation, C<sub>6</sub>H<sub>6</sub> is benzene, BUTD is 1,3-butadiene, MTBE is methyl tertiary-butyl ether, ETOH is ethanol, PAN is peroxyacetyl nitrate, PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates, and HNO<sub>3</sub> is nitric acid.

## B-5. Sensitivity Simulations

Sensitivity analysis is an evaluation of the model response to variations in one or more of the model inputs. Sensitivity simulations were conducted to evaluate the potential impact of using EMFAC2000 (ARB, 1999) instead of EMFAC7G. EMFAC2000 was not available at the time of this study, but emissions from motor vehicles, primarily hydrocarbons, increase substantially with EMFAC2000. A large increase in hydrocarbon emissions will change the NO<sub>x</sub>-to-hydrocarbon ratio and potentially impact the radical flux. This may increase the photochemical oxidation of ethanol and lead to increased acetaldehyde and PAN impacts. For this purpose, hydrocarbon emissions were multiplied by a factor of three to place an upper-limit to the impact of using EMFAC2000, which proposes multiplication factors of 2.34 and 1.84 for the 2000 on-road motor vehicle emission inventory in the South Coast Air Basin for hydrocarbons and NO<sub>x</sub>, respectively. The factor of three is also consistent with an independent fuel-based inventory for the South Coast Air Basin in 1997 which proposes a multiplication factor of 3.5±0.6 for on-road motor vehicle hydrocarbon emissions of stabilized exhaust (Singer and Harley, 1999). The sensitivity simulations considered for this study are listed in Table 5.1. The predicted domain maximum 1-hour-average concentrations from the sensitivity simulations are given in Table 5.2.

**Table 5.1 Sensitivity Scenarios**

Scenario	Description
1997 MTBE Sens	Increased motor vehicle ROG by factor of 3 for the 1997 MTBE fuel
2003 Et3.5% Sens	Increased motor vehicle ROG by factor of 3 for the 2003 Et3.5% fuel
2003 NonOxy Sens	Increased motor vehicle ROG by factor of 3 for the 2003 NonOxy fuel

**Table 5.2 Domain Maximum 1-Hour-Average Concentrations for Sensitivity Simulations**

Sensitivity Simulation	Domain Maximum 1-Hour-Average Concentration (ppb) <sup>a</sup>								
	O <sub>3</sub>	CO	Formalde hyde	Acetalde hyde	C <sub>6</sub> H <sub>6</sub>	BUTD	PAN	PPN	HNO <sub>3</sub>
1997 MTBE Sens	392.2	3,029.8	37.7	19.4	9.1	3.1	18.7	5.7	68.8
2003 Et3.5% Sens	300.4	2,081.0	25.3	14.7	4.7	3.1	11.9	3.6	53.3
2003 NonOxy Sens	298.8	2,265.8	24.5	13.4	4.3	3.1	10.6	3.7	53.6

<sup>a</sup> Formaldehyde and acetaldehyde refer to total concentrations from primary emissions and secondary formation, C<sub>6</sub>H<sub>6</sub> is benzene, BUTD is 1,3-butadiene, PAN is peroxyacetyl nitrate, PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates, and HNO<sub>3</sub> is nitric acid

By comparing Table 4.1 and Table 5.2, it is clear that the predicted domain maximum 1-hour-average concentrations increased significantly for many species when the motor vehicle hydrocarbon emissions were increased by a factor of three. Carbon monoxide, 1,3-butadiene, and nitric acid are notable exceptions. Carbon monoxide concentrations are dominated by direct emissions, so the result is expected. The lack of sensitivity of 1,3-butadiene to hydrocarbon emission increases is presumably due to an increase in its reaction with ozone, which is the dominant loss process for this compound. Nitric acid is formed by reaction of NO<sub>2</sub> with the hydroxyl radical. Hydroxyl radical concentrations increase as ozone increases, so nitric acid concentrations appear to be limited by NO<sub>x</sub> emissions for this summertime episode, especially for the 2003 scenarios.

The 1997 MTBE sensitivity scenario shows a larger increase in maximum concentrations for many species than the 2003 sensitivity scenarios. For example, the predicted maximum 1-hour-average ozone concentration increases by a factor of 1.66 from the 1997 MTBE base case to the 1997 MTBE sensitivity simulation, whereas it only increases by a factor of 1.36 for both 2003 scenarios. Acetaldehyde increases by a factor of 2.11 in 1997 when motor vehicle hydrocarbon emissions are tripled, but it only increases by a factor of 1.52 for the 2003 NonOxy scenario. Similarly, formaldehyde increases by factor of 1.66 for the 1997 MTBE scenario, but only a factor of 1.08 for the 2003 NonOxy scenario. This difference also occurs for benzene, PAN, and PPN. Presumably, these differences are because the motor vehicle emissions are a larger

fraction of the total inventory in 1997 as compared to 2003 (42% of ROG in 1997 versus 30% in 2003).

The major finding is that the predicted maximum 1-hour-average concentrations for acetaldehyde and PAN from the ethanol-containing gasoline (Et3.5%) are now 1.3 ppb greater than the maximum predicted for the non-oxygenated gasoline (NonOxy). These acetaldehyde and PAN impacts from the ethanol-containing gasoline represent an upper limit because the factor of three increase in all on-road hydrocarbon emissions is larger than expected from EMFAC2000 when it becomes final and the ozone episode modeled here is an extreme ozone event.

## B-6. Model Performance

A performance evaluation is the process of establishing that the air quality model is adequately reproducing the chemical and physical processes that generate ozone and other pollutants. One aspect of model performance includes the sensitivity simulations described in Section B-5. In this section we test the model's ability to reproduce measured air quality data. For this purpose, an area and point emission inventory was prepared for a 1987 baseline simulation. Differences and ratios of observed and simulated maximum concentrations were calculated for each day of the August 26-28, 1987 episode in the SCAQS domain. Historical model performance evaluations have focused on ozone, and to a lesser extent, NO<sub>2</sub>. Results are presented for other pollutants under study, including CO, NO, PAN, acetaldehyde, benzene, 1,3-butadiene, and formaldehyde. Although nitric acid data is available from the 1987 SCAQS field program, UAM-FCM does consider the thermodynamic equilibrium of nitric acid with ammonia and ammonium nitrate. We were also unable to conduct a model performance evaluation for ethanol, MTBE, or PPN, as there are no air quality measurements available for these pollutants for the 1987 episode.

### B-6.1. Model Performance Statistics

Several statistical measures were used (ARB, 1992), including the Mean Absolute Gross Error (MAGE):

$$MAGE = \sum \frac{|C_s - C_o|}{N} \quad (B-2)$$

where N is the number of observations, C<sub>s</sub> is the simulated concentration and C<sub>o</sub> is the observed concentration.

Mean Absolute Normalized Gross Error (MANGE):

$$MANGE = \frac{1}{N} \sum \frac{|C_s - C_o|}{C_o} \quad (B-3)$$

Mean Bias (MBIAS):

$$MBIAS = \sum \frac{C_s - C_o}{N} \quad (B-4)$$

Normalized Mean Bias (NBIAS):

$$NBIAS = \frac{1}{N} \sum \frac{C_s - C_o}{C_o} \quad (B-5)$$

and the Unpaired Peak Estimation Accuracy (UPEA):

$$UPEA = \frac{C_s^{\max} - C_o^{\max}}{C_o^{\max}} \quad (B-6)$$

Where  $C_s^{\max}$  is the maximum estimated 1-hour concentration at any site in the domain, and  $C_o^{\max}$  is the maximum observed 1-hour concentration at any site in the domain.

## B-6.2. Ozone, CO, NO, and NO<sub>2</sub>

The average statistics for all sites in the domain are given in Table 6.1 for August 28, 1987 (the last day of the 3-day simulation). The UAM-FCM SAPRC97 tends to over-predict maximum ozone by only 4%. The predicted maximum NO<sub>2</sub> is within 10% of the observed maximum, but the model significantly under-predicts maximum CO and NO, as is typical for grid-based predictions of directly emitted compounds.

**Table 6.1 UAM-FCM with SAPRC97 Model Performance Evaluation**

	O <sub>3</sub> <sup>a</sup>	CO <sup>b</sup>	NO <sup>c</sup>	NO <sub>2</sub> <sup>d</sup>
UPEA (%)	4	-21	-56	7
MBIAS (ppb)	28	-142	-49	-14
MAGE (ppb)	38	771	51	31
NBIAS (%)	32	7	-71	-14
MANGE (%)	38	48	76	60

<sup>a</sup> Only ozone concentrations over 61 ppb were used.

<sup>b</sup> Only CO concentrations over 201 ppb were used.

<sup>c</sup> Only NO concentrations over 21 ppb were used.

<sup>d</sup> Only NO<sub>2</sub> concentrations over 11 ppb were used.

Although the UAM has been widely applied to a number of episodes (see for example, Morris and Meyers, 1990), the UAM-FCM, on the other hand, has had limited application since its development in 1995. Therefore it was considered appropriate to examine the model performance of the UAM-FCM when using a different chemical mechanism, such as the Carbon-Bond IV (CB-IV).

The CB-IV chemical mechanism uses the lumped structure approach to represent the atmospheric oxidation of hydrocarbons in ambient air (Gery *et al.*, 1989). Carbon-bond surrogates are used to represent the chemistry of the three most common type of carbon bonds (single: PAR, double: OLE, and the CHO- group: ALD2), and two molecular surrogates represent the chemistry of aromatic compounds (monoalkylbenzenes: TOL based on toluene; dialkylbenzenes and trialkylbenzenes: XYL based on *m*-xylene). Ethene, isoprene, ethanol, methanol, formaldehyde, methylglyoxal, glyoxal, and PAN are treated explicitly.

Carbon-Bond IV (version 6.21) was implemented into the UAM-FCM. We speciated area and point source emission files, together with initial and boundary conditions for the August 26-28, 1987, for the CB-IV mechanism. Table 6.2 summarizes the performance of the UAM-FCM with CBIV. Compared to the performance of the SAPRC97 mechanism in Table 6.1, CB-IV tends to under-predict maximum ozone concentration by 11% on the last day of the episode. However, both SAPRC97 and CB-IV have similar average performance for CO, NO, and NO<sub>2</sub>. Overall, the UAM-FCM has similar model performance with either SAPRC97 or CB-IV. Figure 6.1 through Figure 6.5 show a comparison of ozone, NO and NO<sub>2</sub>, as predicted by SAPRC97 and CB-IV (together with the measured concentrations), for Anaheim, Burbank, Downtown Los Angeles, and Riverside. Figure 6.5 shows a comparison of ozone, NO, and NO<sub>2</sub>, as predicted by SAPRC97 and CB-IV, for the cell with the maximum pollutant concentration in the domain (no measured data are shown, since there is no monitoring station at this location).

**Table 6.2 UAM-FCM with CB4 Model Performance Evaluation**

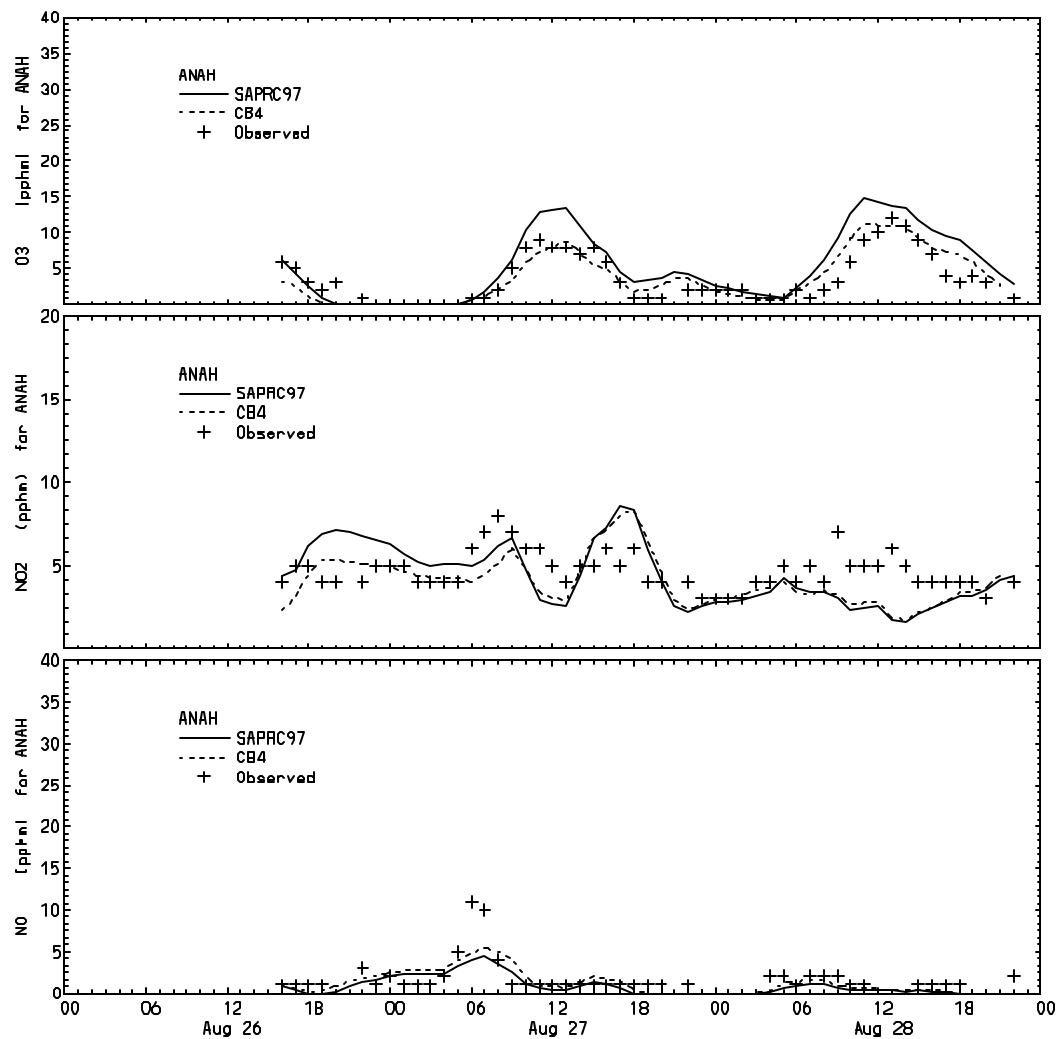
	O <sub>3</sub> <sup>a</sup>	CO <sup>b</sup>	NO <sup>c</sup>	NO <sub>2</sub> <sup>d</sup>
<b>UPEA (%)</b>	<b>-11</b>	<b>-23</b>	<b>-42</b>	<b>0</b>
<b>MBIAS (ppb)</b>	<b>-1</b>	<b>-251</b>	<b>-38</b>	<b>-13</b>
<b>MAGE (ppb)</b>	<b>27</b>	<b>771</b>	<b>45</b>	<b>28</b>
<b>NBIAS (%)</b>	<b>5</b>	<b>0</b>	<b>-50</b>	<b>-12</b>
<b>MANGE (%)</b>	<b>24</b>	<b>46</b>	<b>67</b>	<b>56</b>

**a** Only ozone concentrations over 61 ppb were used.

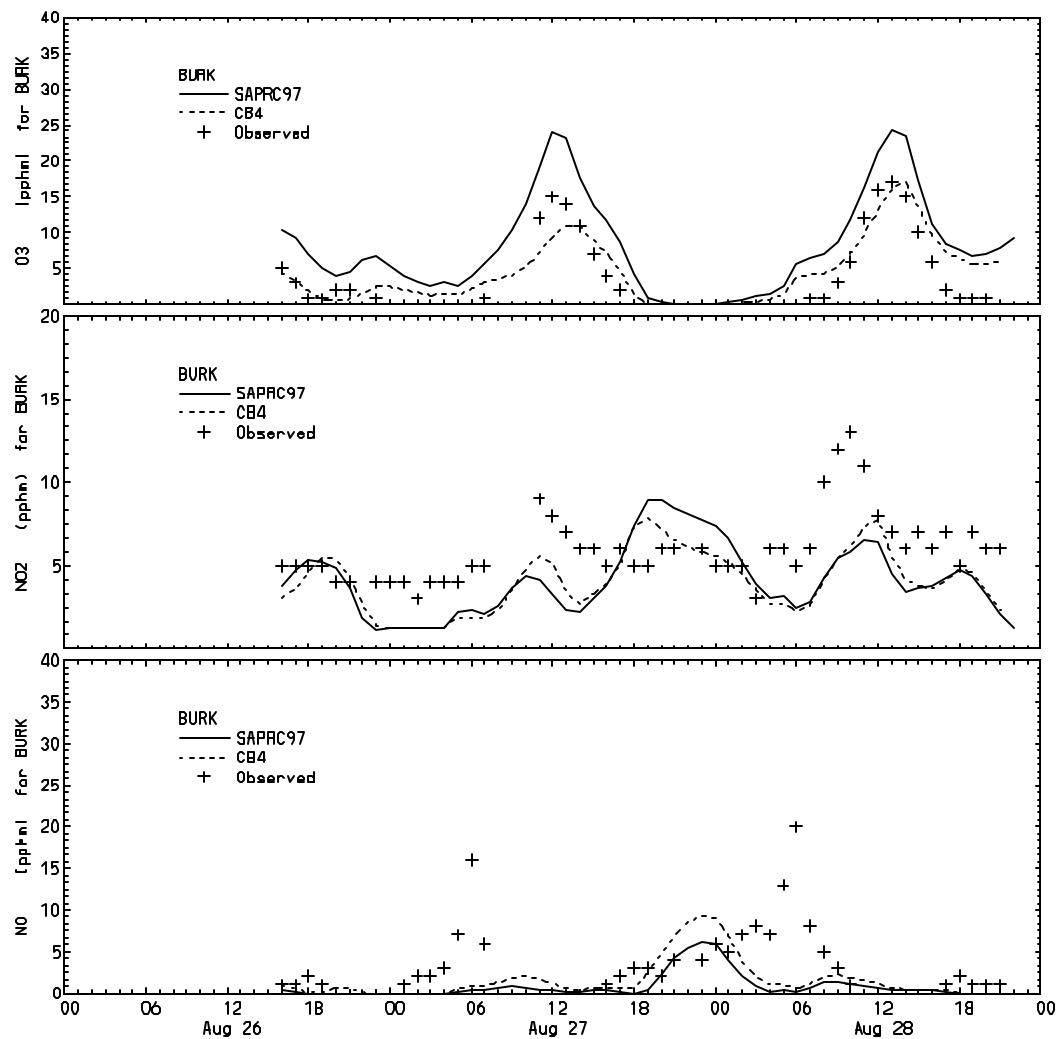
**b** Only CO concentrations over 201 ppb were used.

**c** Only NO concentrations over 21 ppb were used.

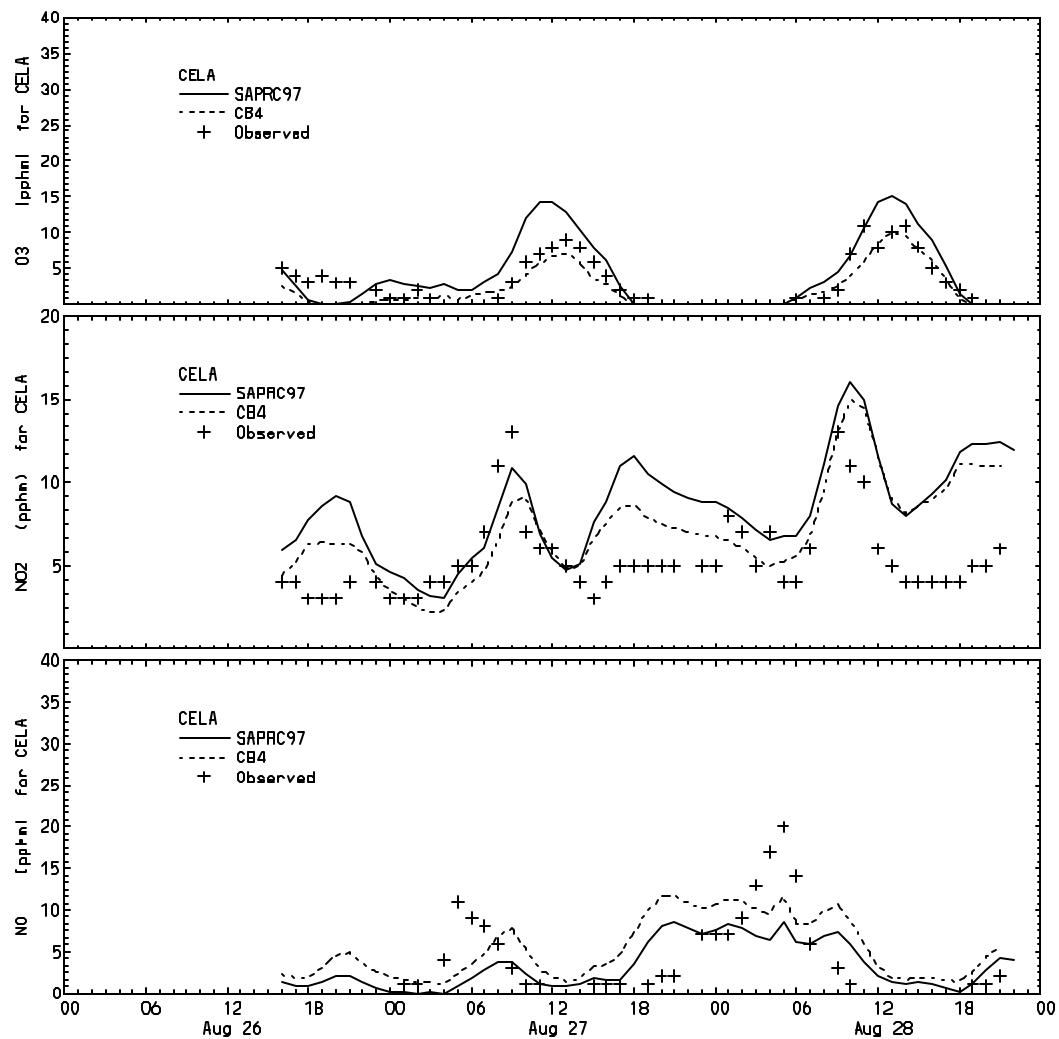
**d** Only NO<sub>2</sub> concentrations over 11 ppb were used.



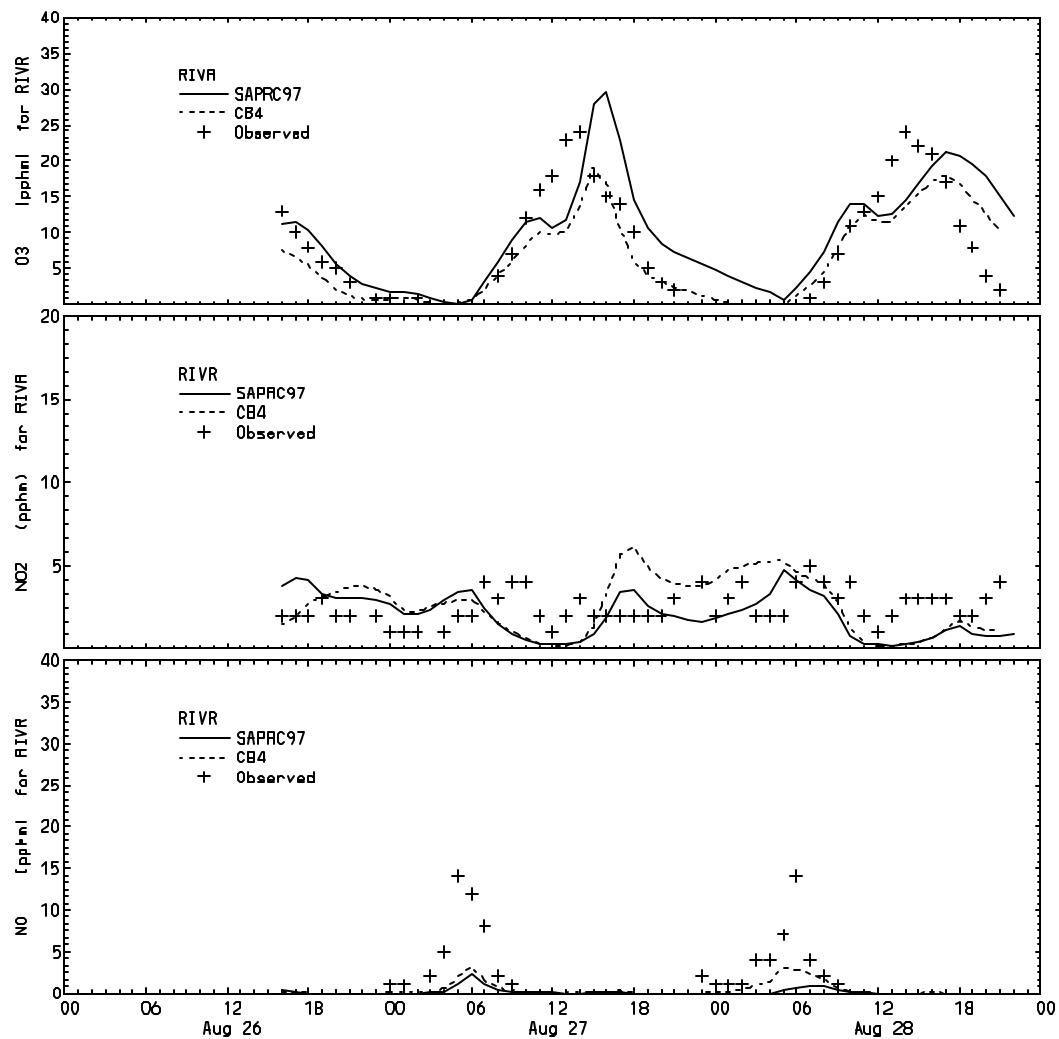
**Figure 6.1 Comparison of Predicted Ozone, NO, and NO<sub>2</sub> by SAPRC97 and CB-IV Against Ambient Data at Anaheim (1987 SCAQS)**



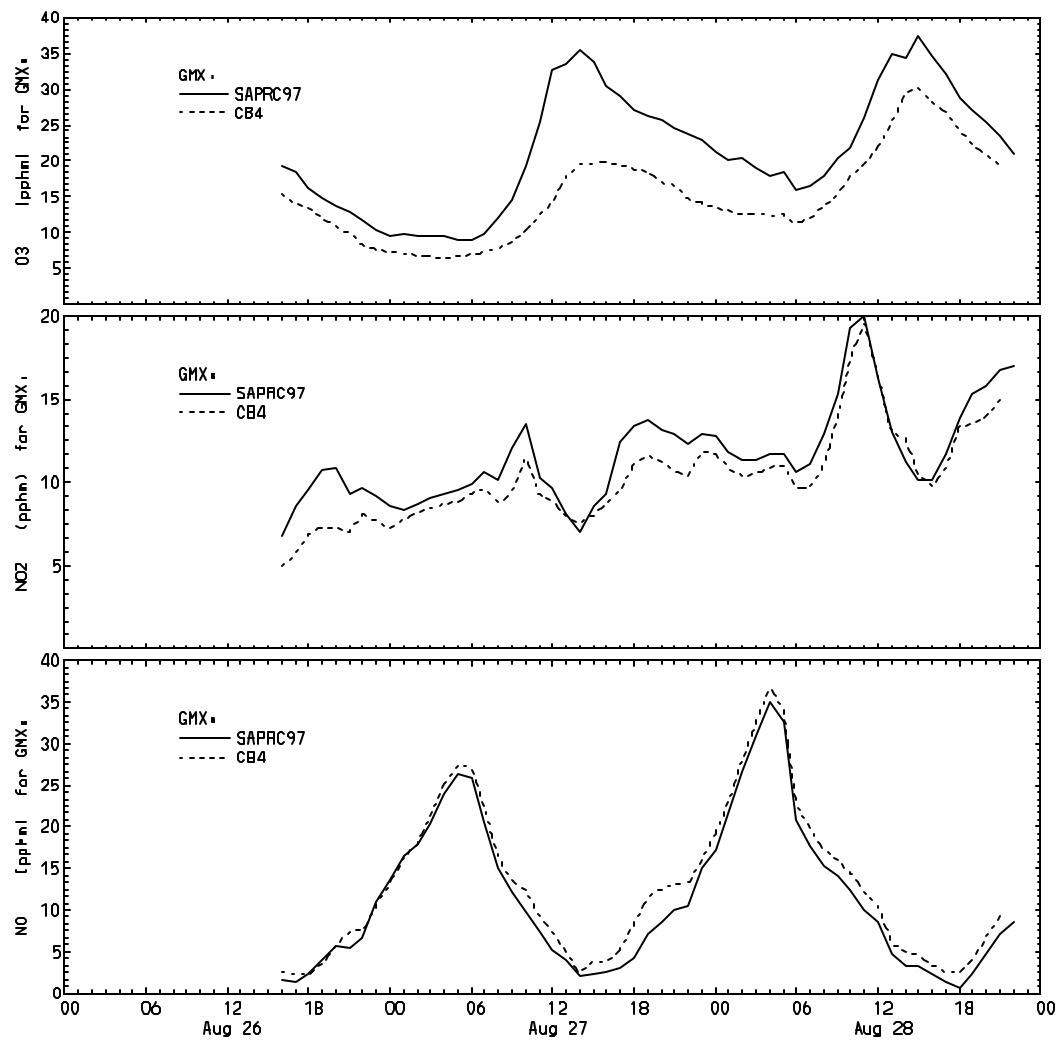
**Figure 6.2 Comparison of Predicted Ozone, NO, and NO<sub>2</sub> by SAPRC97 and CB-IV Against Ambient Data at Burbank (1987 SCAQS)**



**Figure 6.3 Comparison of Predicted Ozone, NO, and NO<sub>2</sub> by SAPRC97 and CB-IV Against Ambient Data at Los Angeles (1987 SCAQS)**



**Figure 6.4 Comparison of Predicted Ozone, NO, and NO<sub>2</sub> by SAPRC97 and CB-IV Against Ambient Data at Riverside (1987 SCAQS)**



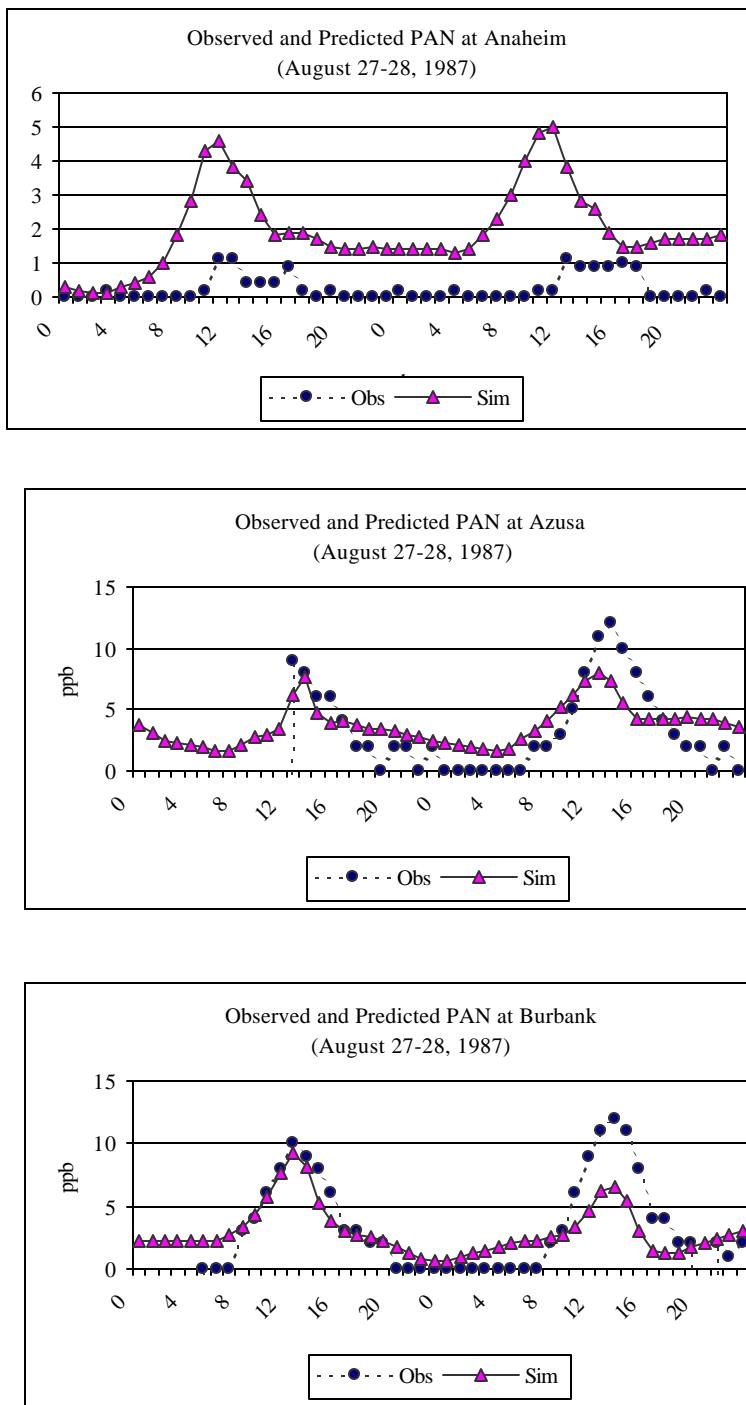
**Figure 6.5 Comparison of Predicted Ozone, NO, and NO<sub>2</sub> by SAPRC97 and CB-IV at the Domain Maximum**

### B-6.3. PAN

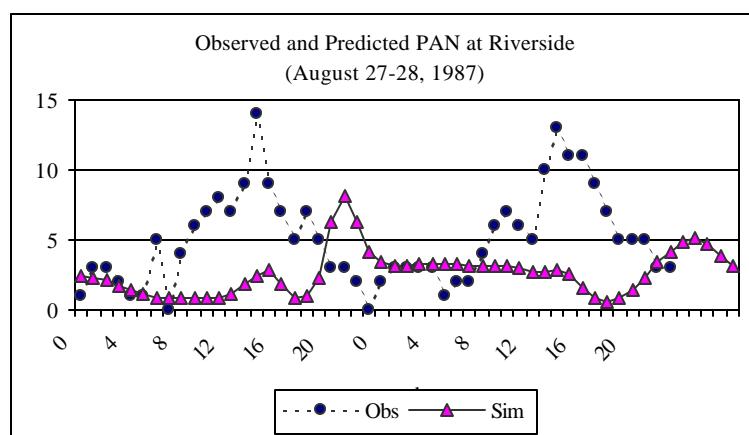
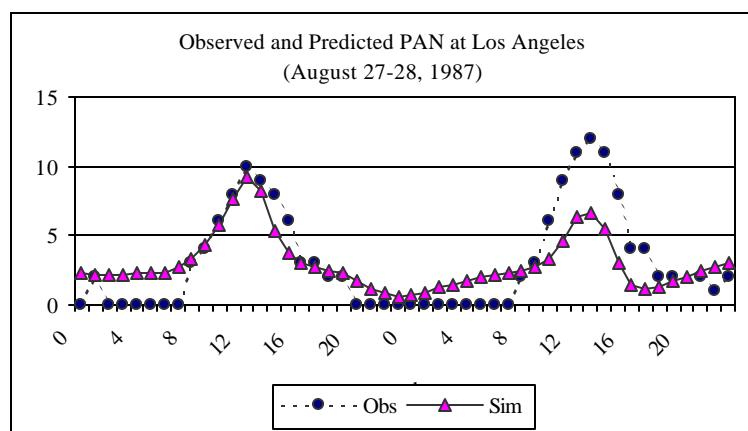
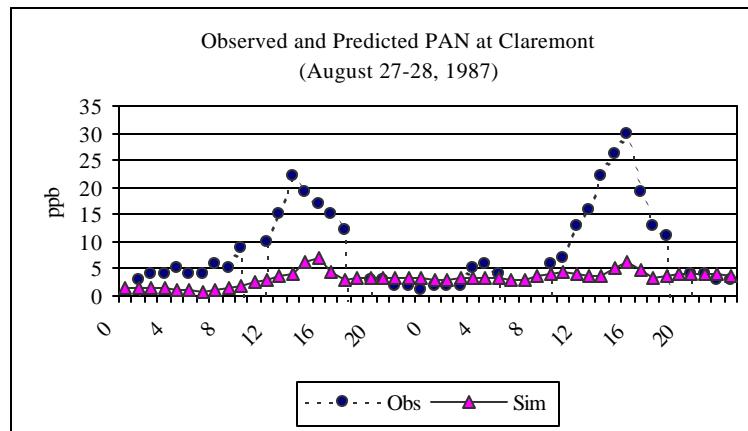
PAN measurements are available at six sites in the SCAQS domain during August 27-28, 1987. Comparisons of hourly PAN concentrations against observations for each site are shown in Figure 6.6 and Figure 6.7. These figures show that, on the last day of the episode, the model under predict PAN concentrations at Burbank, Los Angeles, and, especially, at Claremont and Riverside. However, the model overestimates PAN at Anaheim. Table 6.3 shows the maximum observed and predicted 1-hour-average PAN concentrations. PAN concentrations are sensitive to local variations in the NO to NO<sub>2</sub> ratio and temperature, microscale features that cannot be simulated by gridded models like UAM-FCM.

**Table 6.3 Observed and Predicted Maximum 1-Hour-Average PAN Concentrations for August 28, 1987**

Site	Observed (ppb)	Predicted (ppb)
Anaheim	1.1	5.0
Azusa	12	8.0
Burbank	12	6.6
Claremont	30	6.1
Los Angeles	10	6.0
Riverside	13	5.2



**Figure 6.6 Comparison of Observed and Predicted PAN at Anaheim, Azusa, and Burbank**



**Figure 6.7 Comparison of Observed and Predicted PAN at Claremont, Los Angeles, and Riverside**

### B-6.4. Acetaldehyde, Benzene, 1,3-Butadiene, and Formaldehyde

As an additional evaluation of the air quality model performance, we compared in Table 6.4 the predicted and measured 3-hour-average concentrations for benzene, 1,3-butadiene, total formaldehyde, and total acetaldehyde. Note that concentrations in Table 6.4 are expressed in ppb, and not in ppbC. There are large discrepancies for all species and times between predicted and observed 3-hour-average concentrations at the Los Angeles site. For the other sites, the air quality model predicts a value of the same magnitude as that measured. The discrepancies are most notable during the early morning hours (start time of 6:00 am). However, on average there is better agreement between model predictions and measured data in the late morning (start hour 11:00 am). Overall, the predicted results for acetaldehyde and formaldehyde are in rough agreement with the measurements, while the model severely under-predicts benzene and 1,3-butadiene concentrations. The instantaneous mixing of emissions into a large grid cell by UAM-FCM is a reasonable approximation for secondary pollutants like ozone, NO<sub>2</sub>, acetaldehyde, and formaldehyde, but not for directly emitted pollutants such as benzene and 1,3-butadiene.

**Table 6.4 Measured and Predicted 3-Hour-Average Concentrations for Selected VOCs on August 28, 1987 (ppb)**

Site	Start	Benzene		1,3-Butadiene		Formaldehyde		Acetaldehyde	
		Hour	Measured	Predicted	Measured	Predicted	Measured	Predicted	Measured
Anaheim	600	1.8	2.1	0.3	0.20	6.8	9.8	4.7	4.9
Anaheim	1100	2.6	1.7	0.3	0.00	19.4	11.0	17.4	6.13
Azusa	600	6.0	3.0	1.1	0.30	8.7	17.1	5.8	8.43
Azusa	1100	5.1	2.4	0.1	0.00	19.3	17.4	17.4	10.13
Burbank	600	8.9	1.5	1.5	0.10	8.1	13.0	5.3	5.33
Burbank	1100	6.3	2.9	0.3	0.07	16.8	19.8	15.7	12.1
Los Angeles	600	37.6	4.6	2.1	0.77	7.8	15.4	3.5	7.9
Los Angeles	1100	5.9	4.3	0.2	0.13	10.0	26.1	9.9	16.6
Hawthorne	600	1.2	1.6	0.1	0.23	3.0	6.4	3.1	3.57
Hawthorne	1100	0.6	1.6	0.1	0.10	4.9	7.7	4.1	4.73
Long Beach	600	5.0	3.8	0.5	0.57	11.3	10.4	5.5	5.5
Long Beach	1100	2.8	3.4	0.1	0.10	13.9	16.0	12.5	11.67
Riverside	600	5.9	2.6	0.7	0.10	8.5	18.1	5.7	9.07
Riverside	1100	2.5	0.7	0.1	0.00	13.3	6.8	13.2	3.2
Average (600)		9.5	2.8	0.9	0.3	7.7	12.9	4.8	6.4
Average (1100)		3.7	2.4	0.2	0.1	13.9	15.0	12.9	9.2
Average (600 & 1100)		6.6	2.6	0.5	0.2	10.8	13.9	8.8	7.8

## B-7. Ozone, PAN, and PPN Formation Potentials

In addition to the 3-dimensional airshed model simulations, we also investigated the ozone, PAN, and PPN (which includes higher molecular weight acyl peroxy nitrates) formation potentials for each of the explicit VOCs and lumped species in the SAPRC97 chemical mechanism. This was used to explain the lack of sensitivity of PAN formation to the ethanol content of the gasoline observed in Section B-4.

### B-7.1. Description of Formation Potentials

The formation of secondary pollutants in an airshed is a complex process, which involves a series of photochemical reactions driven by the sunlight. It has been recognized that individual organic compounds can contribute differently to the creation of secondary air pollutants in atmosphere. Over decades, a variety of scales of VOC formation potential have been devised to quantify the degree to which different organic compounds affect formation of a given pollutant, such as ozone. More generally, the potential of a given organic compound in atmospheric chemistry refers to the reactivity of that compound to promote formation of products. Among these scales, the incremental reactivity developed by Carter and Atkinson (1989) is the simplest method of calculating the potential of an organic compound to form ozone or any other pollutant.

Given a  $VOC_i$ , its ozone incremental reactivity is defined as the ratio of the ozone concentration change to a small perturbation of the  $VOC_i$ :

$$\text{Ozone formation potential} = \lim_{\Delta VOC_i \rightarrow 0} \left[ \frac{O_3(VOC_i + \Delta VOC_i) - O_3(VOC_i)}{\Delta VOC_i} \right] \quad (\text{B-7})$$

where  $O_3(VOC_i + \Delta VOC_i)$  and  $O_3(VOC_i)$  are the ozone concentrations of the perturbed case and base case of  $VOC_i$ , respectively. Yang *et al.* (1995) show that ozone formation potential can be estimated as the local sensitivity of the predicted ozone concentration to the initial concentrations of each organic compound in a mixture.

Similarly, the PAN formation potential of a given organic compound,  $VOC_i$ , in a mixture or airshed can be calculated by:

$$\text{PAN formation potential} = \lim_{\Delta VOC_i \rightarrow 0} \left[ \frac{PAN(VOC_i + \Delta VOC_i) - PAN(VOC_i)}{\Delta VOC_i} \right] \quad (\text{B-8})$$

where  $PAN(VOC_i + \Delta VOC_i)$  and  $PAN(VOC_i)$  are the PAN concentrations of the perturbed case and base case of  $VOC_i$ , respectively. The equation, in essence, is a local sensitivity of PAN to the concentration change of an organic compound and can be computed by the partial differentiation of PAN with respect to  $VOC_i$ . The PAN sensitivity coefficient, i.e.,

$$\frac{\partial PAN}{\partial VOC_i}$$

is interpreted as the amount of PAN formed per unit amount of VOC<sub>i</sub> changed in the mixture and has units of ppm-PAN/ppm-VOC or ppm-PAN/ppm-C.

The total formation potential for ozone, PAN, and PPN can be calculated by using a first-order approximation:

$$\text{Total PAN formation potential} = \sum_i \left( \frac{\partial \text{PAN}}{\partial \text{VOC}_i} \right) \Delta \text{VOC}_i \quad (\text{B-9})$$

## B-7.2. Model Description and Inputs

The scenario for the ozone, PAN, and PPN formation potential calculations is adopted from the average condition of 39 cities across the U.S. designed by Carter (1994) for ozone incremental reactivity. Pollutant formation potential scales are time varying over the 10-hour simulation. The results presented here are the formation potentials of ozone, PAN, and PPN estimated at 1800 where the maximum ozone occurs in the simulation period, because the time satisfies the condition of maximum incremental reactivity scale (Yang *et al.*, 1995).

We implemented the SAPRC97 chemical mechanism -- as described in Attachment B1 -- in a box model to evaluate the ozone, PAN, and PPN formation potential of selected individual VOCs and lumped VOC categories. Table 7.1 gives the PAN and PPN reactions, together with the value of their corresponding kinetic parameters (as used in the box model). Table 7.2 provides the default meteorological inputs for the box-model simulations. Table 7.3 gives the initial conditions for several episodes in the South Coast Air Basin, and Table 7.4 has the initial conditions for episodes representative of two large cities in Brazil.

**Table 7.1 PAN and PPN Equilibrium Reaction Rate Constants**

Reactions	$\text{CCO-O}_2 + \text{NO}_2 = \text{PAN}$	$\text{PAN} = \text{CCO-O}_2 + \text{NO}_2 + \text{RCO}_3$	$\text{C}_2\text{CO-O}_2 + \text{NO}_2 = \text{PPN}$	$\text{PPN} = \text{C}_2\text{CO-O}_2 + \text{NO}_2 + \text{RCO}_3$
Kinetic	$A_0 = 2.57 \times 10^{-28}$	$A_0 = 4.9 \times 10^{-3}$	$A = 8.4 \times 10^{-12}$	$A = 1.6 \times 10^{17}$
Parameters	$E_0 = 0.0$	$E_0 = 23.972$	$E = 0.0$	$E = 27.966$
	$B_0 = -7.1$	$B_0 = 0.0$	$B = 0.0$	$B = 0.0$
	$A_i = 12.0 \times 10^{-12}$	$A_i = 4.0 \times 10^{16}$		
	$E_i = 0.0$	$E_i = 27.079$		
	$B_i = -0.9$	$B_i = 0.0$		
	$F = 0.3$	$F = 0.3$		
	$N = 1.0$	$N = 1.0$		
$k(298^\circ\text{K})$	$3.3 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	$3.9 \times 10^{-2} \text{ min}^{-1}$	$1.2 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	$4.1 \times 10^{-2} \text{ min}^{-1}$

Note: All kinetic parameters in cm-molecules · sec units. PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates (see Attachment B1).

**Table 7.2 Meteorological Inputs<sup>a</sup>**

Time	Temperature ( $^\circ\text{K}$ )	Mixing Height (m)	Zenith Angle (degrees) <sup>b</sup>
800	295.5	292.9	71.6
900	297.7	595.7	59.5
1000	299.9	998.5	47.5
1100	301.8	1201	35.9
1200	303.3	1503	25.9
1300	304.5	1610	20.1
1400	305.6	1716	22.1
1500	305.8	1823	30.4
1600	306.1	1823.1	41.3
1700	305.9	1823.2	53.1
1800	305.1	1823.3	65.2

<sup>a</sup> Adopted from the average scenario of 39 cities, Carter (1994).

<sup>b</sup> Evaluated at the latitude of  $36.22^\circ$  and the solar declination of  $16.5^\circ$  (Los Angeles)

**Table 7.3 Initial Concentrations for South Coast Air Basin Scenarios (ppm)**

Initial Concentrations	South Coast <sup>b</sup> 1968	Los Angeles <sup>c</sup> 1968	LARPP <sup>d</sup> 1973	Los Angeles 8/28/87 <sup>a</sup>	SCAQS 8/28/87 <sup>a</sup>	Los Angeles 12/3/87 <sup>a</sup>	Claremont <sup>f</sup> 9/8/93	Azusa <sup>e</sup> 8/6/97	Azusa <sup>e</sup> 10/4/97	Azusa <sup>e</sup> 8/22/97
O <sub>3</sub>	0.01	0.01	0.01	0.0067	0.01	0.01	0.04	0.02	0.0043	0.001
NO	0.24	0.341	0.034	0.1	0.04	0.19	0.18	0.031	0.05	0.141
NO <sub>2</sub>	0.049	0.069	0.007	0.05	0.05	0.06	0.12	0.104	0.065	0.072
CO	10.3	10.3	1.91	5.4	2.0	6.64	4.0	2.64	2.53	3.1
Methane	3.3	3.3	2.01	2.62	2.6	3.44	2.6	2.82	2.58	2.6
Ethene	0.065	0.076	-	0.0526	0.027	0.036	0.018	0.028	0.026	0.0301
Formaldehyde	0.005	0.005	0.01	0.008	0.005	0.011	-	0.011	0.0074	0.0003
Acetaldehyde	0.005	0.005	0.005	0.0035	0.005	0.0067	-	0.006	0.0028	0.0009
Acetone	-	-	-	0.057	-	0.0083	-	0.016	0.0075	0.0007
MEK	-	-	-	0.0008	-	0.0032	-	0.005	0.001	0.0003
Benzene	-	-	-	0.038	0.0078	0.011	0.0029	-	0.013	0.0025
Isoprene	-	-	-	0.0008	-	0.0005	-	0.000	0.0008	0.0041
Ethanol	-	-	-	-	-	-	-	-	-	-
MTBE	-	-	-	-	-	-	-	-	-	-
1,3 Butadiene	-	0.0028	-	-	-	-	0.0003	-	-	0.00018
Dichloromethane	-	-	-	-	0.001	-	0.014	0.0004	0.000	-
ALK1 (lumped alkanes, $k_{OH} < 1.0 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$ )	0.37	0.455	0.286	0.506	0.18	0.245	0.081	0.373	0.24	0.078
ALK2 (lumped alkanes, $k_{OH} \geq 1.0 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$ )	0.038	0.039	0.021	0.18	0.018	0.014	0.0094	0.13	0.083	0.014
ARO1 (lumped aromatics, $k_{OH} < 2.0 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$ )	0.033	0.06	0.024	0.206	0.06	0.034	0.0068	0.083	0.068	0.011
ARO2 (lumped aromatics)	0.044	0.081	0.02	0.11	0.081	0.019	0.0058	0.089	0.051	0.007
OLE1 (lumped terminal alkenes, $k_{OH} \geq 2.0 \times 10^4$ $\text{ppm}^{-1} \text{ min}^{-1}$ )	0.016	0.036	0.023	0.094	0.036	0.108	0.004	0.023	0.075	0.0076
OLE2 (lumped internal alkenes)	-	0.02	0.017	0.0098	0.02	0.005	0.0022	0.019	0.01	0.0026
OLE3 (terpenes)	-	-	-	-	-	-	0.00017	-	-	0.0041
ROG/NO <sub>x</sub>	8.3	8.3	3.1	44	13.3	6.8	1.6	30.8	25.1	3.05

<sup>a</sup>Lawson, 1990<sup>d</sup>Calvert, 1976<sup>b</sup>Lonemann, 1968<sup>e</sup>McCauley, 1999<sup>c</sup>Kopczynski, 1968<sup>f</sup>Pasek, 1999Note: Other constant concentrations are included in the simulation runs, i.e., CO<sub>2</sub>, O<sub>2</sub>, Air, and H<sub>2</sub>.

**Table 7.4 Initial Concentrations for Brazil Scenarios (ppm)**

Initial Concentrations	Porto Alegre, Brazil 1998 <sup>a</sup>	Avenida Brazil, Rio de Janeiro 1999 <sup>b</sup>
O <sub>3</sub>	0.01	0.01
NO	0.143	0.22
NO <sub>2</sub>	0.029	0.045
CO	3.34	5.1
Methane	0.86	0.0012
Ethene	0.036	0.056
Formaldehyde	0.0124	0.0097
Acetaldehyde	0.014	0.0102
Acetone	-	-
MEK	-	-
Benzene	0.038	0.068
Isoprene	0.0042	-
Ethanol	0.012	0.0485
MTBE	0.066	-
1,3 Butadiene	0.062	0.012
Dichloromethane	-	-
ALK1 (lumped alkanes, $k_{OH} < 1.0 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$ )	0.315	1.03
ALK2 (lumped alkanes, $k_{OH} \geq 1.0 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$ )	0.2	0.57
ARO1 (lumped aromatics, $k_{OH} < 2.0 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$ )	0.12	0.245
ARO2 (lumped aromatic)	0.22	0.515
OLE1 (lumped terminal alkenes, $k_{OH} \geq 2.0 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$ )	0.061	0.075
OLE2 (lumped internal alkenes)	0.10	0.164
OLE3 (terpenes)	-	-
ROG/NO <sub>X</sub>	44.5	67.0

<sup>a</sup> Grosjean *et al.* (1998)<sup>b</sup> Grosjean (1999)Note: Other constant concentrations are included in the simulation runs, i.e., CO<sub>2</sub>, O<sub>2</sub>, Air, and H<sub>2</sub>.

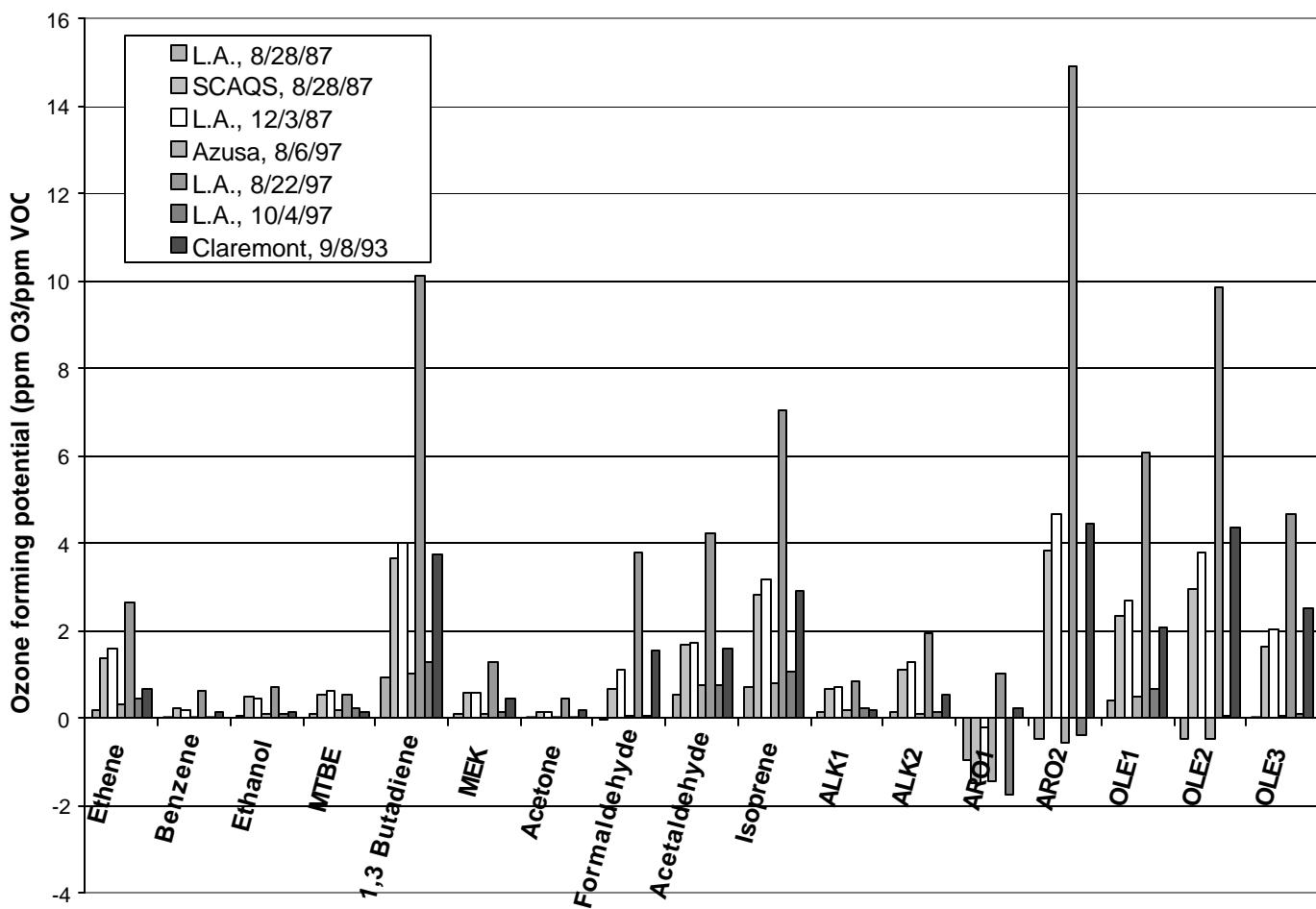
### B-7.3. Results

Figure 7.1 and Figure 7.2 present the individual ozone formation potentials for the twelve cases described in Table 7.3 and Table 7.4. Note that all box model simulations were conducted with all VOC and NO<sub>x</sub> inputs as initial conditions, i.e., no emissions over the simulation time period. This is a reasonable approach for a Lagrangian model that simulates an air parcel as it travels over a region, but will likely underestimate the contribution from fast-reacting species in comparison to more slowly reacting compounds (e.g., alkanes, ethanol). The ranking has a general consistency with relatively high ozone formation potentials for ethene, 1,3-butadiene, formaldehyde, acetaldehyde, isoprene, ARO2, and the three lumped olefin classes. However, the ozone formation potential for ARO1 tends to be negative across the cases. Previous studies have shown that aromatic compounds could have negative ozone reactivity under some high-VOC loading conditions (Carter, 1994; Khan *et al.*, 1998).

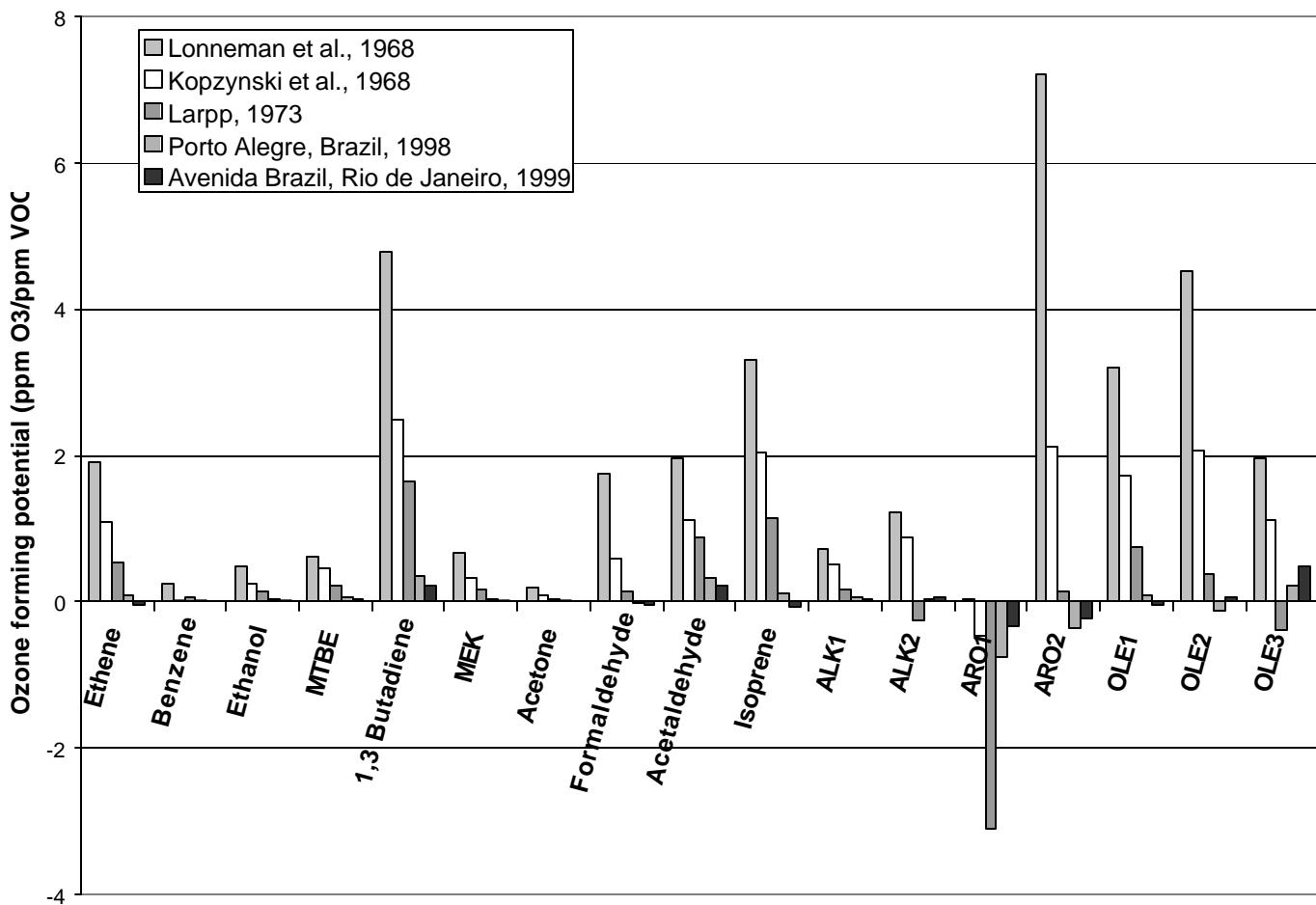
For PAN production, 1,3-butadiene, acetaldehyde, isoprene, ARO2, and the three lumped olefin classes have relatively high formation potential compared to other compounds, as shown in Figure 7.3 and Figure 7.4. As with ozone, the ARO1 class was found to have negative formation potential for most simulated cases. For the ten explicit VOC compounds in the figures, the rank of PAN formation potentials estimated here has general agreement with a recent study by Derwent *et al.* (1998). Figure 7.5 and Figure 7.6 show that 1,3-butadiene, acetaldehyde, isoprene, and the three lumped olefin classes have higher PPN formation potentials. For most simulated cases, ARO1 and ARO2 have negative potential for PPN production.

The total ozone formation potentials for the ten explicit VOCs are given in Table 7.5 and Table 7.6. The total PAN formation potentials are provided in Table 7.7 and Table 7.8, and the total PPN formation potentials are shown in Table 7.9 and Table 7.10. For the Los Angeles cases in the last 1960s and early 1970s, the lumped alkane class ALK1 is the main contributor to ozone, PAN, and PPN concentrations. The lumped aromatic class ARO2 also contributes significantly for these historical cases. For the more recent cases in the 1980s and 1990s, ALK1 remains a large contributor, but the role of ARO2 diminishes and the contribution of the lumped olefin classes increase. This shift most likely reflects the effects of a decreasing aromatic content in gasoline and diesel fuel.

In the two Brazilian cases, ALK1 is the major contributor to ozone and PAN concentrations are dominated by ARO2, OLE1, and OLE2. OLE2 is the major contributor to PPN. Even though ethanol and acetaldehyde concentrations are relatively high, they are not the major contributors to PAN. Thus, the box model simulations are consistent with the results from the three-dimensional airshed model that ethanol substitution scenarios will not necessarily lead to a substantial increase in PAN concentrations.



**Figure 7.1 Ozone Formation Potentials From Individual VOCs**



**Figure 7.2 Ozone Formation Potentials From Individual VOCs (continued)**

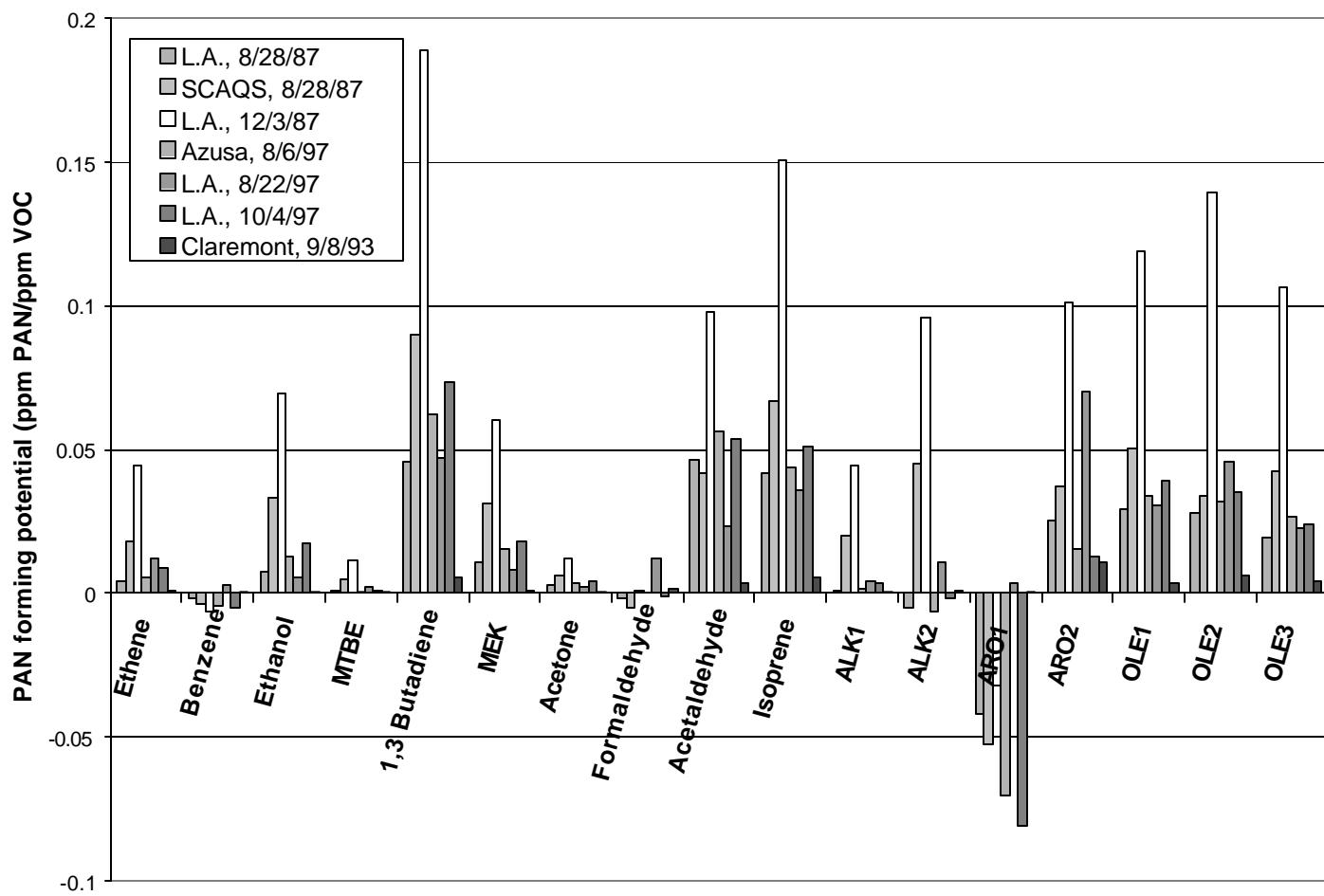


Figure 7.3 PAN Formation Potentials From Individual VOCs

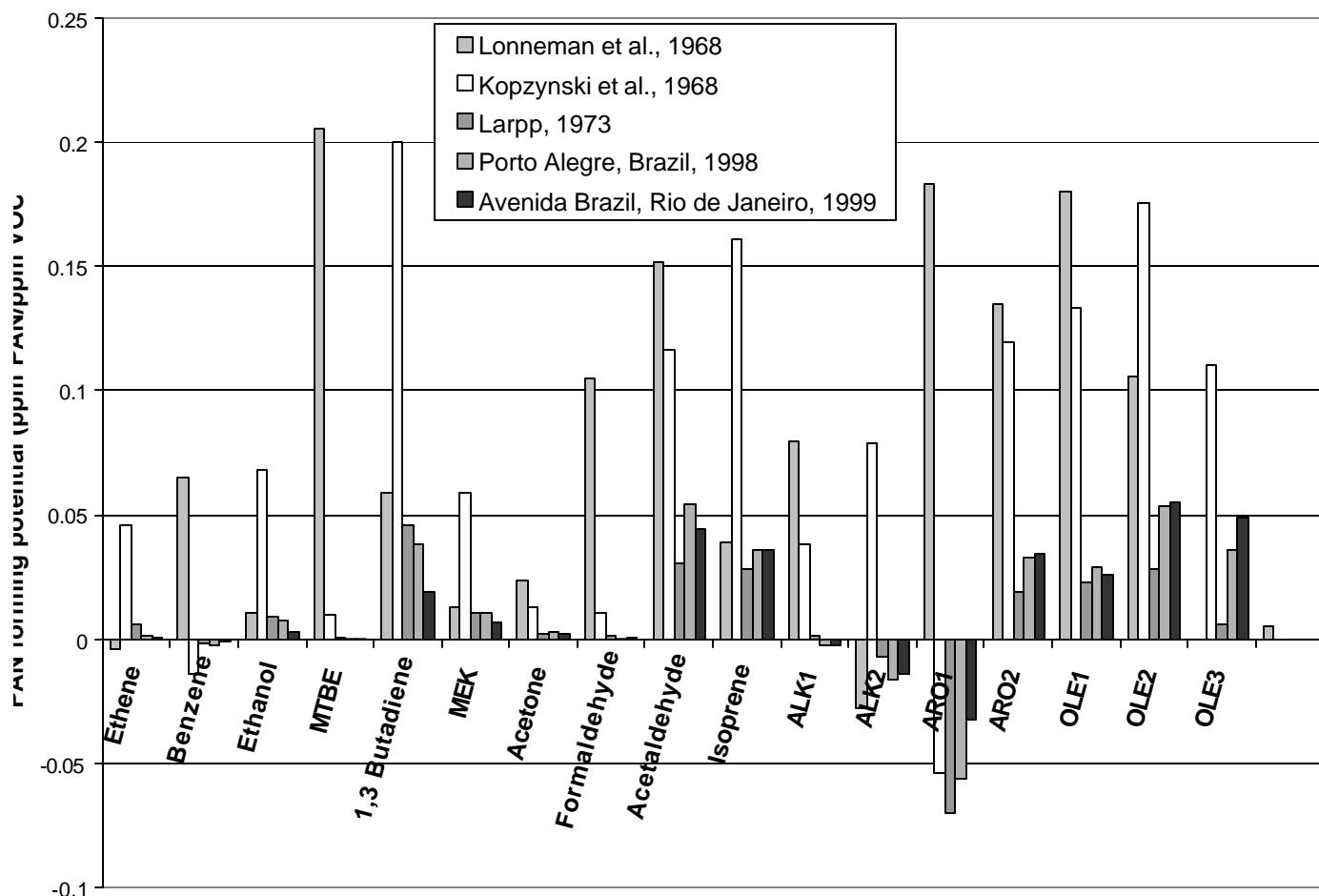


Figure 7.4 PAN Formation Potentials From Individual VOCs (continued)

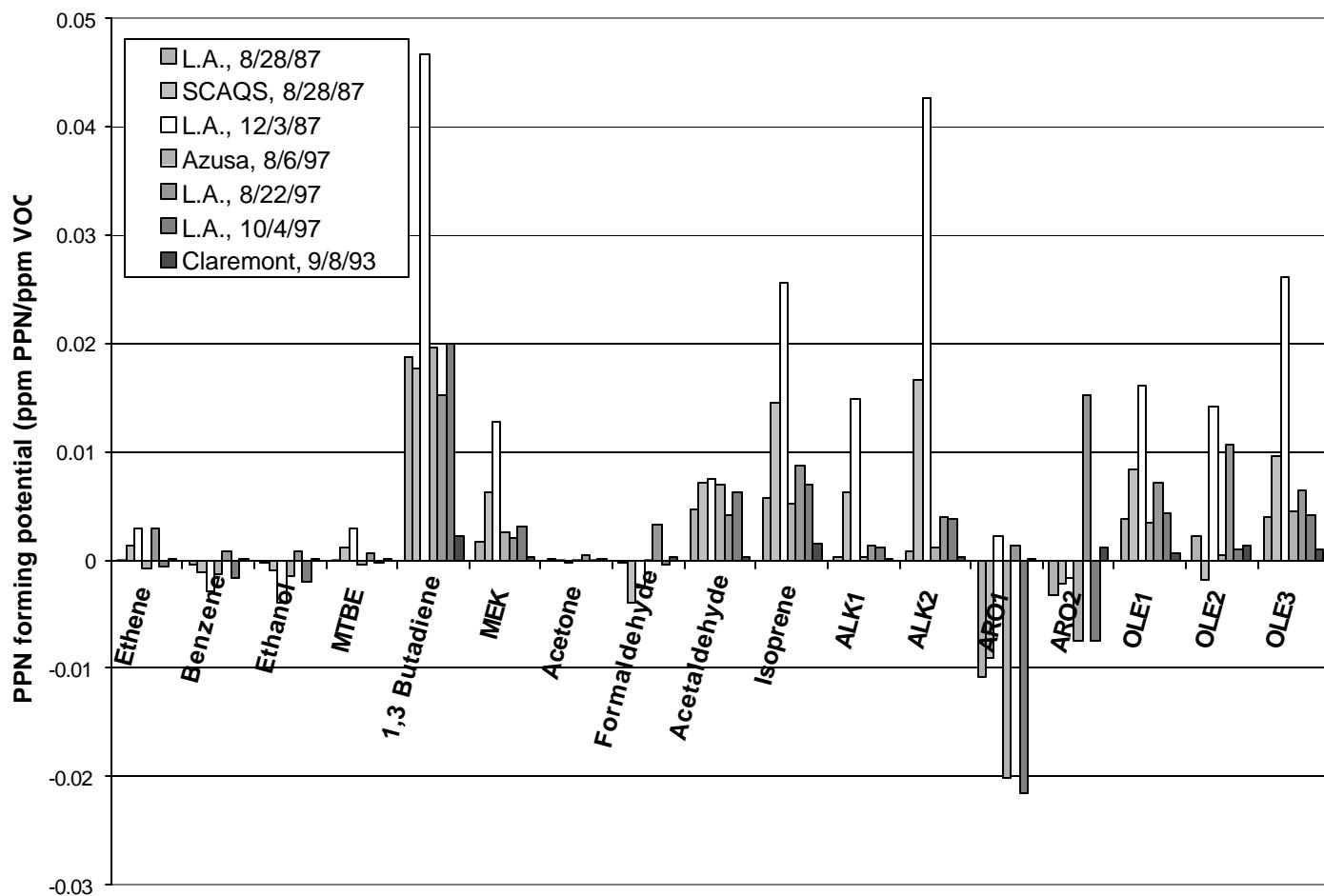


Figure 7.5 PPN Formation Potentials From Individual VOCs

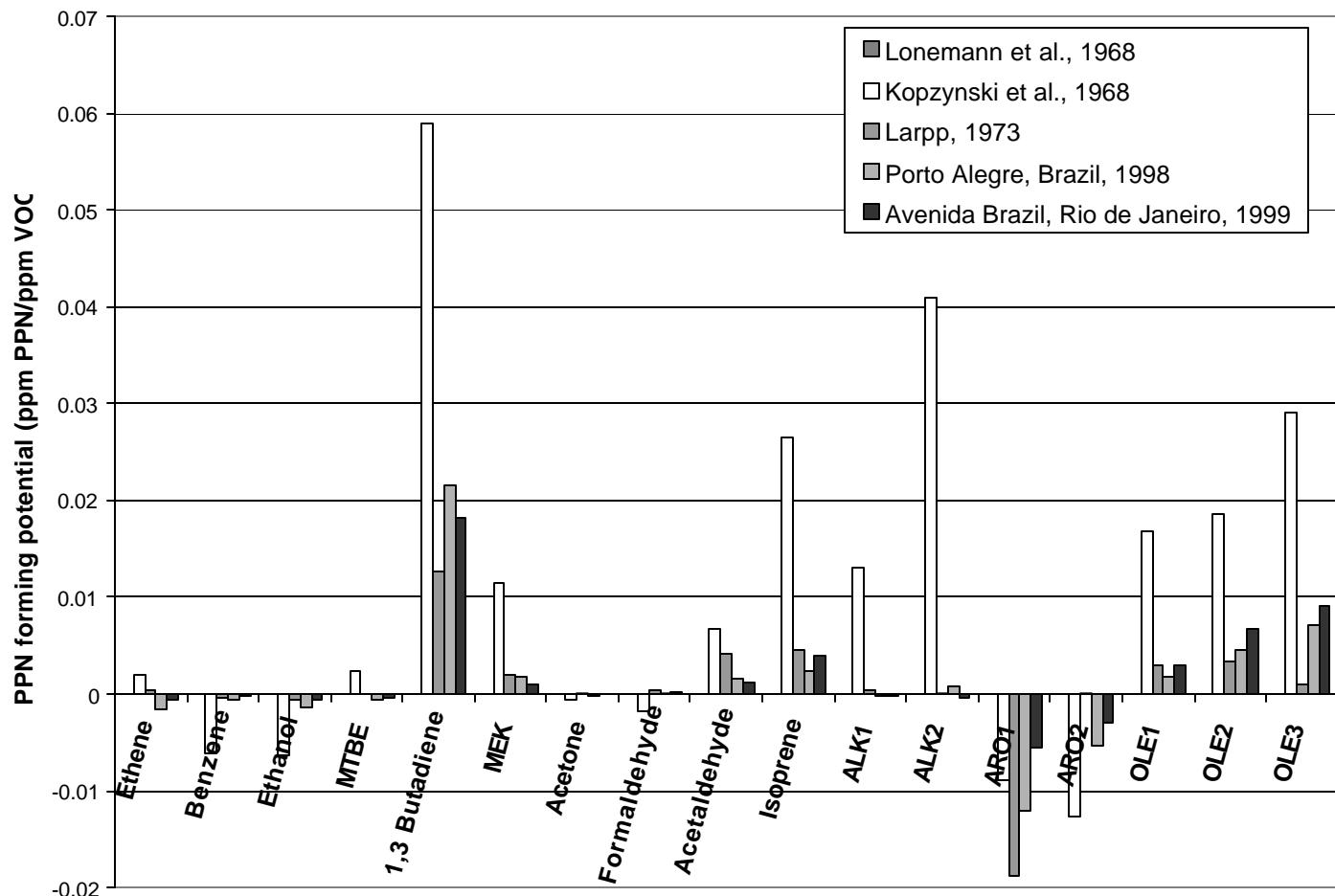


Figure 7.6 PPN Formation Potentials From Individual VOCs (continued)

**Table 7.5 Total Ozone Formation Potentials<sup>\*</sup> From Individual VOCs (ppm)**

VOCs	South Coast <sup>b</sup> 1968	Los Angeles <sup>c</sup> 1968	LARPP <sup>d</sup> 1973	Los Angeles 8/28/87 <sup>a</sup>	SCAQs 8/28/87 <sup>a</sup>	Los Angeles 12/3/87 <sup>a</sup>	Claremont <sup>f</sup> 9/8/93	Azusa <sup>e</sup> 8/6/97	Los Angeles <sup>e</sup> 10/4/97	Los Angeles <sup>e</sup> 8/22/97
Ethene	0.124	0.082		0.010	0.036	0.057	0.013	0.009	0.012	0.08
Benzene				0.00032	0.0019	0.002	0.00043		0.0003	0.0015
Ethanol										
MTBE										
1,3-Butadiene		0.007					0.0011			0.0018
MEK				<0.0001		0.0018		0.00062	0.00014	0.0004
Acetone				<0.0001		0.0012		0.00034	0.0002	0.0003
Formaldehyde	0.0087	0.003	0.0014	-0.0004	0.0035	0.012		0.0004	0.00053	0.0011
Acetaldehyde	0.01	0.0056	0.0044	0.0012	0.0084	0.011		0.0047	0.002	0.004
Isoprene				0.0006		0.0016		0.00073	0.0009	0.030
ALK1	0.26	0.24	0.047	0.067	0.12	0.18	0.017	0.063	0.051	0.065
ALK2	0.047	0.034	-0.005	0.028	0.019	0.018	0.005	0.014	0.01	0.027
ARO1	0.001	-0.028	-0.075	-0.2	-0.026	-0.007	0.0016	-0.12	-0.12	0.011
ARO2	0.32	0.17	0.003	-0.052	0.071	0.09	0.026	-0.05	-0.02	0.1
OLE1	0.051	0.063	0.018	0.036	0.016	0.29	0.008	0.011	0.051	0.046
OLE2		0.042	0.0065	-0.0047		0.019	0.009	-0.009	0.00036	0.026
OLE3							0.0004			0.019

$$^* \text{TOFP} = \sum_i (OFP_i)(VOC_i^o)$$

<sup>a</sup> Lawson, 1990<sup>d</sup> Calvert, 1976<sup>b</sup> Lonemann, 1968<sup>e</sup> McCauley<sup>c</sup> Kopczynski, 1968<sup>f</sup> Pasek, 1999

**Table 7.6 Total Ozone Formation Potentials<sup>\*</sup> From Individual VOCs (ppm)**

VOCs	Porto Alegre, Brazil	Avenida Brazil, Rio de Janeiro
	1998 <sup>a</sup>	1999 <sup>b</sup>
Ethene	0.003	-0.002
Benzene	0.00044	0.00015
Ethanol	0.00032	0.00071
MTBE	0.00049	
1,3-Butadiene	0.0022	0.0027
MEK		
Acetone		
Formaldehyde	-0.0003	-0.00034
Acetaldehyde	0.005	0.0023
Isoprene	0.0005	
ALK1	0.023	0.044
ALK2	0.0054	0.03
ARO1	-0.089	-0.08
ARO2	-0.08	-0.12
OLE1	0.005	-0.0021
OLE2	-0.011	0.013
OLE3		

$$^* \text{TOFP} = \sum_i (OFP_i)(VOC_i^o)$$

<sup>a</sup> Grosjean *et al.* (1998)

<sup>b</sup> Grosjean (1999)

**Table 7.7 Total PAN Formation Potentials<sup>\*</sup> From Individual VOCs (ppm)**

VOCs	South Coast <sup>b</sup> 1968	Los Angeles <sup>c</sup> 1968	LARPP <sup>d</sup> 1973	Los Angeles 8/28/87 <sup>a</sup>	SCAQs 8/28/87 <sup>a</sup>	Los Angeles 12/3/87 <sup>a</sup>	Claremont <sup>f</sup> 9/8/93	Azusa <sup>e</sup> 8/6/97	Los Angeles <sup>e</sup> 10/4/97	Los Angeles <sup>e</sup> 8/22/97
Ethene	0.0035	0.0035		0.00023	0.00049	0.0016	<0.0001	0.00016	0.00036	0.0002
Benzene				>0.0001	>0.0001	>0.0001	<0.0001		<0.0001	>0.0001
Ethanol										
MTBE										
1,3-Butadiene		0.0006					<0.0001		<0.0001	
MEK				<0.0001		0.0002		<0.0001	<0.0001	<0.0001
Acetone				<0.0001		0.0001		<0.0001	<0.0001	<0.0001
Formaldehyde	0.0001	<0.0001	<0.0001	>0.0001	>0.0001	<0.0001		0.0000003	<0.0001	>0.0001
Acetaldehyde	0.0005	0.0006	0.00015	0.00016	0.0002	0.0007		0.00035	<0.0001	0.00015
Isoprene				<0.0001		<0.0001		<0.0001	0.00015	<0.0001
ALK1	0.014	0.017	0.00033	0.00052	0.0037	0.011	<0.0001	0.0005	0.00036	<0.0001
ALK2	0.003	0.0031	-0.00015	-0.0009	0.0008	0.0014	<0.0001	-0.0009	0.00015	-0.00012
ARO1	-0.0009	-0.0033	-0.0017	-0.0087	-0.0009	-0.0011	<0.0001	-0.0058	<0.0001	-0.0055
ARO2	0.008	0.0097	0.00038	0.0028	0.0007	0.002	<0.0001	0.0014	0.0005	0.00067
OLE1	0.0022	0.0049	0.00053	0.0027	0.0004	0.013	<0.0001	0.0008	0.0002	0.0029
OLE2		0.0035	0.0005	0.00027		0.0007	<0.0001	0.0006	0.00012	0.00035
OLE3							<0.0001		<0.0001	

$$* \text{TPANFP} = \sum_i (PANFP_i)(VOC_i^o)$$

<sup>a</sup>Lawson, 1990<sup>d</sup>Calvert, 1976<sup>b</sup>Lonemann, 1968<sup>e</sup>McCauley, 1999<sup>c</sup>Kopczynski, 1968<sup>f</sup>Pasek, 1999

**Table 7.8 Total PAN Formation Potentials<sup>\*</sup> From Individual VOCs (ppm)**

VOCs	Porto Alegre, Brazil	Avenida Brazil, Rio de Janeiro
	1998 <sup>a</sup>	1999 <sup>b</sup>
Ethene	<0.0001	<0.0001
Benzene	>0.0001	>0.0001
Ethanol	<0.0001	0.00015
MTBE	>0.0001	
1,3-Butadiene	0.00024	0.0002
MEK		
Acetone		
Formaldehyde	>0.0001	<0.0001
Acetaldehyde	0.00075	0.00045
Isoprene	0.00015	
ALK1	-0.0007	-0.0026
ALK2	-0.003	-0.008
ARO1	-0.0065	-0.008
ARO2	0.007	0.018
OLE1	0.0018	0.0019
OLE2	0.005	0.009
OLE3		

$$* \text{ TPANFP} = \sum_i (PANFP_i)(VOC_i^o)$$

<sup>a</sup> Grosjean *et al.*, 1998

<sup>b</sup> Grosjean, 1999

**Table 7.9 Total PPN Formation Potentials<sup>a,b</sup> From Individual VOCs (ppm)**

VOCs	Los Angeles 8/28/87 <sup>c</sup>	SCAQs 8/28/87 <sup>c</sup>	Los Angeles 12/3/87 <sup>c</sup>	Azusa <sup>g</sup> 8/6/97	Los Angeles <sup>g</sup> 10/4/97	Los Angeles <sup>g</sup> 8/22/97	Claremont <sup>h</sup> 9/8/93	South Coast <sup>d</sup> 1968	Los Angeles <sup>e</sup> 1968	LARPP <sup>f</sup> 1973
Ethene	>0.0001	<0.0001	0.0001	>0.0001	<0.0001	>0.0001	<0.0001	0.00037	0.00016	
Benzene	>0.0001	>-0.0001	>0.0001		<0.0001	>0.0001	<0.0001			
Ethanol										
MTBE										
1,3 Butadiene					<0.0001		<0.0001		0.00016	
MEK	<0.0001		<0.0001	<0.0001	<0.0001	<0.0001				
Acetone	<0.0001		>0.0001	>0.0001	<0.0001	>0.0001				
Formaldehyde	>0.0001	>0.0001	>0.0001	>0.0001	<0.0001	>0.0001		>0.0001	>0.0001	<0.0001
Acetaldehyde	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001		<0.0001	<0.0001	<0.0001
Isoprene	<0.0001		<0.0001	<0.0001	<0.0001	<0.0001				
ALK1	0.00015	0.001	0.0036	<0.0001	0.0001	0.00026	<0.0001	0.0052	0.006	0.000117
ALK2	0.00014	0.0003	0.0006	0.00015	<0.0001	0.00031	<0.0001	0.0016	0.0016	<0.0001
ARO1	-0.002	-0.00016	<0.0001	-0.002	<0.0001	-0.0015	<0.0001	>0.0001	-0.0005	-0.00045
ARO2	-0.0004	>0.0001	>0.0001	-0.0007	0.0001	-0.0004	<0.0001	0.00027	-0.001	<0.0001
OLE1	0.00035	<0.0001	0.002	<0.0001	<0.0001	0.00032	<0.0001	0.00032	0.0006	<0.0001
OLE2	<0.0001		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001		0.00038	<0.0001
OLE3					<0.0001		<0.0001			

$$^a \text{TPPNFP} = \sum_i (PPNFP_i)(VOC_i^o).$$

<sup>b</sup>Note that PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates

<sup>c</sup>Lawson, 1990

<sup>f</sup>Calvert, 1976

<sup>d</sup>Lonemann, 1968

<sup>g</sup>McCauley, 1999

<sup>e</sup>Kopczynski, 1968

<sup>h</sup>Pasek, 1999

**Table 7.10 Total PPN Formation Potentials<sup>a,b</sup> From Individual VOCs (ppm)**

VOCs	Porto Alegre, Brazil	Avenida Brazil, Rio de Janeiro
	1998 <sup>c</sup>	1999 <sup>d</sup>
Ethene	>0.0001	>0.0001
Benzene	>0.0001	>0.0001
Ethanol	>0.0001	>0.0001
MTBE	>0.0001	
1,3-Butadiene	0.00013	0.0002
MEK		
Acetone		
Formaldehyde	<0.0001	<0.0001
Acetaldehyde	<0.0001	<0.0001
Isoprene	<0.0001	
ALK1	>0.0001	-0.0003
ALK2	0.00016	-0.0003
ARO1	-0.001	-0.0014
ARO2	-0.0011	-0.0015
OLE1	0.00011	0.00023
OLE2	0.00047	0.001
OLE3		

$$\text{a} \quad \text{TPPNFP} = \sum_i (PPNFP_i)(VOC_i^o)$$

b Note that PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates

c Grosjean *et al.* (1998)

d Grosjean (1999)

#### B-7.4. Other Study of PAN Formation Potentials

The PAN formation potential results in Table 7.7 and Table 7.8 are in agreement with the results obtained by Bowman and Seinfeld (1994) for the relative contribution of lumped VOC species to PAN formation. From Table 7.11, ALK1, ALK2, ARO2, and OLE1 have large contributions to PAN formation, while acetaldehyde has a low contribution to PAN formation.

**Table 7.11 Relative Contribution of Lumped VOC Species to PAN Formation<sup>a</sup>**

Species	Description <sup>b</sup>	Initial Concentration <sup>d</sup> (ppbC)	Contribution to PAN <sup>d</sup> (%)
CO	Carbon monoxide	1,500	-
CH4	Methane	1,700	-
HCHO	Formaldehyde	8	-
CCHO	Acetaldehyde	5	2.6
RCHO	Higher molecular weight aldehydes	2	0.5
MEK	Higher molecular weight ketones	16	1.4
ALK1	Low molecular weight alkanes	353	18.6
ALK2	Higher molecular weight alkanes	236	13.5
ARO1	Benzene and toluene	147	9.4
ARO2	Higher molecular weight aromatics (mostly xylenes)	108	15.2
ETHE	Ethylene	75	6.8
OLE1	Low molecular weight, less reactive alkenes	60	14.9
OLE2	Low molecular weight, more reactive alkenes	29	8.9
OLE3	Biogenic compounds (isoprene + terpenes)	62	8.3

<sup>a</sup> Adapted from Bowman and Seinfeld (1994)<sup>b</sup> SAPRC90 (Carter, 1990)<sup>c</sup> Using 1987 SCAQS emission inventory as input data<sup>d</sup> At VOC/NO<sub>x</sub>=8.2 ppbC/ppb

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## Attachment B1 – Listing of SAPRC97 Chemical Mechanism

This attachment provides a listing of the SAPRC97 mechanism. Separate listings are provided for the isoprene reaction mechanism and for other species treated explicitly in Attachments B2 and B3, respectively. Interpretation of reactions rates constants can be found in Kumar *et al.* (1996). Note that this chemical mechanism contains explicit gas-phase reactions for some organic compounds, such as formaldehyde, acetaldehyde, ethylene, and PAN. However, the PPN model species represents higher acyl peroxy nitrates (e.g., CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CO-OO-NO<sub>2</sub>), but not alkyl peroxy nitrates such as CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-OO-NO<sub>2</sub>. The latter are not represented in the model because of their rapid back-decomposition to reactants at ambient temperatures. PPN does not represent the aromatic acyl peroxy nitrates that are represented by the PBZN model species (Carter, 1990 and 1999a). In the newest version of update to the mechanism, SAPRC99, Carter (1999b) uses PAN2 instead of PPN.

```

1)      PF=NO2          ;NO2 + HV = NO + O
2) 6.0E-34, 0.0, -2.3   ;O + O2 + M = O3 + M
3A) 6.5E-12, -0.238    ;O + NO2 = NO + O2
!
3B)      FALLOFF        ;O + NO2 = NO3 + M
9.0E-32 0.0 -2.0
2.2E-11 0.0  0.0
0.6   1.0
!
4) 2.00E-12, 2.782     ;O3 + NO = NO2 + O2
5) 1.400E-13, 4.968    ;O3 + NO2 = O2 + NO3
6) 1.7E-11, -0.298     ;NO + NO3 = #2 NO2
7) 3.300E-39, -1.05    ;NO + NO + O2 = #2 NO2
!
8)      FALLOFF        ;NO2 + NO3 = N2O5
2.2E-30 0.0 -4.3
1.5E-12 0.0 -0.5
0.6   1.0
!
9) 9.09E+26, 22.26     ;N2O5 + #RCON8 = NO2 + NO3
10) 1.0E-21 0.0         ;N2O5 + H2O = #2 HNO3
11) 2.5E-14, 2.44       ;NO2 + NO3 = NO + NO2 + O2
12A)     PF=NO3NO       ;NO3 + HV = NO + O2
12B)     PF=NO3NO2      ;NO3 + HV = NO2 + O
13A)     PF=O3O3P       ;O3 + HV = O + O2
13B)     PF=O3O1D       ;O3 + HV = O*1D2 + O2
14) 2.2E-10,   0.0       ;O*1D2 + H2O = #2 HO
15) 1.919E-11, -0.251   ;O*1D2 + M = O + M
!
16)      FALLOFF        ;HO + NO = HONO
7.0E-31 0.0 -2.6
1.5E-11 0.0 -0.5
0.6   1.0
!
17)     PF=HONO         ;HONO + HV = HO + NO

```

!

18) FALLOFF ;HO + NO<sub>2</sub> = HNO<sub>3</sub>  
 2.6E-30 0.0 -3.2  
 2.4E-11 0.0 -1.3  
 0.6 1.0

!

19) 6.45E-15, -1.652 ;HO + HNO<sub>3</sub> = H<sub>2</sub>O + NO<sub>3</sub> ! 1 ATM ONLY.  
 21) 2.4E-13, 0.0 ;HO + CO = HO<sub>2</sub> + CO<sub>2</sub> !1 ATM ONLY  
 22) 1.600E-12, 1.87 ;HO + O<sub>3</sub> = HO<sub>2</sub> + O<sub>2</sub>  
 23) 3.700E-12, -0.48 ;HO<sub>2</sub> + NO = HO + NO<sub>2</sub>

!

24) FALLOFF ;HO<sub>2</sub> + NO<sub>2</sub> = HNO<sub>4</sub>  
 1.8E-31 0.0 -3.2  
 4.7E-12 0.0 -1.4  
 0.6 1.0

!

25) 4.76E+26, 21.66 ;HNO<sub>4</sub> + #RCO24 = HO<sub>2</sub> + NO<sub>2</sub>  
 27) 1.3E-12, -0.755 ;HNO<sub>4</sub> + HO = H<sub>2</sub>O + NO<sub>2</sub> + O<sub>2</sub>  
 28) 1.100E-14, 0.994 ;HO<sub>2</sub> + O<sub>3</sub> = HO + #2 O<sub>2</sub>  
 29A) 2.2E-13, -1.23 ;HO<sub>2</sub> + HO<sub>2</sub> = H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub>  
 29B) 1.9E-33, -1.95 ;HO<sub>2</sub> + HO<sub>2</sub> + M = H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub>  
 29C) 3.1E-34, -5.60 ;HO<sub>2</sub> + HO<sub>2</sub> + H<sub>2</sub>O = H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub> + H<sub>2</sub>O  
 !29D) 2.7E-54, -6.32 ;HO<sub>2</sub> + HO<sub>2</sub> + M + H<sub>2</sub>O = H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub> + H<sub>2</sub>O  
 29D) 6.6E-35, -6.32 ;HO<sub>2</sub> + HO<sub>2</sub> + H<sub>2</sub>O = H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub> + H<sub>2</sub>O !(1 ATM ONLY)  
 30A) 2.2E-13, -1.23 ;NO<sub>3</sub> + HO<sub>2</sub> = HNO<sub>3</sub> + O<sub>2</sub>  
 30B) 1.9E-33, -1.95 ;NO<sub>3</sub> + HO<sub>2</sub> + M = HNO<sub>3</sub> + O<sub>2</sub>  
 30C) 3.1E-34, -5.60 ;NO<sub>3</sub> + HO<sub>2</sub> + H<sub>2</sub>O = HNO<sub>3</sub> + O<sub>2</sub> + H<sub>2</sub>O  
 30D) 6.6E-35, -6.32 ;NO<sub>3</sub> + HO<sub>2</sub> + H<sub>2</sub>O = HNO<sub>3</sub> + O<sub>2</sub> + H<sub>2</sub>O  
 31) PF=H<sub>2</sub>O<sub>2</sub> ;H<sub>2</sub>O<sub>2</sub> + HV = #2 HO  
 32) 3.300E-12, 0.397 ;H<sub>2</sub>O<sub>2</sub> + HO = HO<sub>2</sub> + H<sub>2</sub>O  
 33) 4.60E-11, -0.457 ;HO + HO<sub>2</sub> = H<sub>2</sub>O + O<sub>2</sub>  
 B1) 4.200E-12, -0.360 ;RO<sub>2</sub> + NO = NO

!

B2) FALLOFF ;RCO<sub>3</sub> + NO = NO  
 5.65E-28 0.0 -7.1  
 2.64E-11 0.0 -0.9  
 0.27 1.0

!

B4) FALLOFF ;RCO<sub>3</sub> + NO<sub>2</sub> = NO<sub>2</sub>  
 2.57E-28 0.0 -7.1  
 12.0E-12 0.0 -0.9  
 0.30 1.0

!

B5) 3.40E-13, -1.590 ;RO<sub>2</sub> + HO<sub>2</sub> = HO<sub>2</sub>  
 B6) 3.40E-13, -1.590 ;RCO<sub>3</sub> + HO<sub>2</sub> = HO<sub>2</sub>  
 B8) 1.0E-15 ;RO<sub>2</sub> + RO<sub>2</sub> =  
 B9) 1.86E-12, -1.053 ;RO<sub>2</sub> + RCO<sub>3</sub> =  
 B10) 2.8E-12, -1.053 ;RCO<sub>3</sub> + RCO<sub>3</sub> =  
 B11) SAMEK B1 ;RO<sub>2</sub>-R + NO = NO<sub>2</sub> + HO<sub>2</sub>  
 B12) SAMEK B5 ;RO<sub>2</sub>-R + HO<sub>2</sub> = XOOH  
 B13) SAMEK B8 ;RO<sub>2</sub>-R + RO<sub>2</sub> = RO<sub>2</sub> + #.5 HO<sub>2</sub>  
 B14) SAMEK B9 ;RO<sub>2</sub>-R + RCO<sub>3</sub> = RCO<sub>3</sub> + #.5 HO<sub>2</sub>  
 B19) SAMEK B1 ;RO<sub>2</sub>-N + NO = RNO<sub>3</sub>  
 B20) SAMEK B5 ;RO<sub>2</sub>-N + HO<sub>2</sub> = XOOH + MEK + #1.5 XC  
 B21) SAMEK B8 ;RO<sub>2</sub>-N + RO<sub>2</sub> = RO<sub>2</sub> + #.5 HO<sub>2</sub> + MEK + #1.5 XC  
 B22) SAMEK B9 ;RO<sub>2</sub>-N + RCO<sub>3</sub> = RCO<sub>3</sub> + #.5 HO<sub>2</sub> + MEK + #1.5 XC

B15) SAMEK B1 ;R2O2 + NO = NO2  
 B16) SAMEK B5 ;R2O2 + HO2 =  
 B17) SAMEK B8 ;R2O2 + RO2 = RO2  
 B18) SAMEK B9 ;R2O2 + RCO3 = RCO3  
 B23) SAMEK B1 ;RO2-XN + NO = XN  
 B24) SAMEK B5 ;RO2-XN + HO2 = XOOH  
 B25) SAMEK B8 ;RO2-XN + RO2 = RO2 + #.5 HO2  
 B26) SAMEK B9 ;RO2-XN + RCO3 = RCO3 + HO2  
 G2) SAMEK B1 ;RO2-NP + NO = NPHE  
 G3) SAMEK B5 ;RO2-NP + HO2 = XOOH + #6 XC  
 G4) SAMEK B8 ;RO2-NP + RO2 = RO2 + #.5 HO2 + #6 XC  
 G5) SAMEK B9 ;RO2-NP + RCO3 = RCO3 + HO2 + #6 XC  
 B7) PF=CO2H ;XOOH + HV = HO2 + HO  
 B7A) 1.18E-12, -0.254 ;HO + XOOH = HO  
 B7B) 1.79E-12, -0.435 ;HO + XOOH = RO2-R + RO2  
 C1) PF=HCHONEWR ;HCHO + HV = #2 HO2 + CO  
 C2) PF=HCHONEWM ;HCHO + HV = H2 + CO  
 C3) 1.125E-12 -1.288 2.0 ;HCHO + HO = HO2 + CO + H2O  
 C4) 9.7E-15, -1.242 ;HCHO + HO2 = HOCOO  
 C4A) 2.4E+12, 13.91 ;HOCOO = HO2 + HCHO  
 C4B) SAMEK B1 ;HOCOO + NO = XC + NO2 + HO2  
 C9) 2.8E-12, 5.00 ;HCHO + NO3 = HNO3 + HO2 + CO  
 C10) 5.55E-12, -0.618 ;CCHO + HO = CCO-O2 + H2O + RCO3  
 C11A) PF=CCHOR ;CCHO + HV = CO + HO2 + HCHO + RO2-R + RO2  
 C12) 1.4E-12, 3.696 ;CCHO + NO3 = HNO3 + CCO-O2 + RCO3  
 C25) 8.5E-12 -0.50 ;RCHO + HO = C2CO-O2 + RCO3  
 C26) PF=RCHO ;RCHO + HV = CCHO + RO2-R + RO2 + CO + HO2  
 C27) 1.4E-12, 3.696 ;NO3 + RCHO = HNO3 + C2CO-O2 + RCO3  
 C38) 4.81E-13 0.457 2.0 ;ACET + HO = R2O2 + HCHO + CCO-O2 + RCO3 + RO2  
 C39) PF=ACET-93C ;ACET + HV = CCO-O2 + HCHO + RO2-R + RCO3 + RO2  
 C44) 2.92E-13 -0.823 2.0 ;MEK + HO = H2O + #.5 "CCHO + HCHO + CCO-O2 + &  
 C57) PF=KETONE ;C2CO-O2 " + RCO3 + #1.5 "R2O2 + RO2"  
 C95) 2.191E-11, 1.408 ;MEK + HV + #0.1 = CCO-O2 + CCHO + RO2-R + RCO3 &  
 C13) SAMEK B2 ;+ RO2  
 C14) SAMEK B4 ;RNO3 + HO = NO2 + #.155 MEK + #1.05 RCHO + &  
 C15) SAMEK B6 ;#.48 CCHO + #.16 HCHO + #.11 XC + #1.39 "R2O2 + RO2 "  
 C16) SAMEK B9 ;CCO-O2 + NO = CO2 + NO2 + HCHO + RO2-R + RO2  
 C17) SAMEK B10 ;CCO-O2 + NO2 = PAN  
 ! ;CCO-O2 + HO2 = XOOH + CO2 + HCHO  
 C18) FALLOFF ;CCO-O2 + RO2 = RO2 + #.5 HO2 + CO2 + HCHO  
 4.90E-03 23.972 0.0 ;CCO-O2 + RCO3 = RCO3 + HO2 + CO2 + HCHO  
 4.00E+16 27.079 0.0  
 0.30 1.00  
 ! ;PAN = CCO-O2 + NO2 + RCO3  
 C28) SAMEK B2 ;C2CO-O2 + NO = CCHO + RO2-R + CO2 + NO2 + RO2  
 C29) 8.4E-12 0.0 0.0 ;C2CO-O2 + NO2 = PPN  
 C30) SAMEK B6 ;C2CO-O2 + HO2 = XOOH + CCHO + CO2  
 C31) SAMEK B9 ;C2CO-O2 + RO2 = RO2 + #.5 HO2 + CCHO + CO2  
 C32) SAMEK B10 ;C2CO-O2 + RCO3 = RCO3 + HO2 + CCHO + CO2  
 C33) 1.6E+17, 27.966 ;PPN = C2CO-O2 + NO2 + RCO3  
 TBON) 2.4E-11 ;C2(C)-O + NO2 = RNO3 + #2 XC  
 TBOD) 7.5E+14, 16.2 ;C2(C)-O = ACET + HCHO + RO2-R + RO2  
 C58A) PF=GLYOXAL1 ;GLY + HV = #.8 HO2 + #.45 HCHO + #1.55 CO

C58B) PF=GLYOXAL2 ;GLY + HV + #.029 = #.13 HCHO + #1.87 CO  
 C59) 1.14E-11 ;GLY + HO = #.6 HO2 + #1.2 CO + #.4 "HCOCO-O2 + &  
       RCO3 "  
 C60) SAMEK C12 ;GLY + NO3 = HNO3 + #.6 HO2 + #1.2 CO + &  
       #.4 "HCOCO-O2 + RCO3 "  
 C62) SAMEK B2 ;HCOCO-O2 + NO = NO2 + CO2 + CO + HO2  
 C63) SAMEK B4 ;HCOCO-O2 + NO2 = GPAN  
 C64) SAMEK C18 ;GPAN = HCOCO-O2 + NO2 + RCO3  
 C65) SAMEK B6 ;HCOCO-O2 + HO2 = XOOH + CO2 + CO  
 C66) SAMEK B9 ;HCOCO-O2 + RO2 = RO2 + #.5 HO2 + CO2 + CO  
 C67) SAMEK B10 ;HCOCO-O2 + RCO3 = RCO3 + HO2 + CO2 + CO  
 C68A) PF=MEGLYOX1 ;MGLY + HV = HO2 + CO + CCO-O2 + RCO3  
 C68B) PF=MEGLYOX2 ;MGLY + HV + #.107 = HO2 + CO + CCO-O2 + RCO3  
 C69) 1.72E-11 ;MGLY + HO = CO + CCO-O2 + RCO3  
 C70) SAMEK C12 ;MGLY + NO3 = HNO3 + CO + CCO-O2 + RCO3  
 G46) 2.63E-11 ;HO + PHEN = #.15 RO2-NP + #.85 RO2-R + #.2 GLY + &  
       #4.7 XC + RO2  
 G51) 3.6E-12 ;NO3 + PHEN = HNO3 + BZ-O  
 G52) 4.2E-11 ;HO + CRES = #.15 RO2-NP + #.85 RO2-R + #.2 MGLY + &  
       #5.5 XC + RO2  
 G57) 2.1E-11 ;NO3 + CRES = HNO3 + BZ-O + XC  
 G30) 1.29E-11 ;BALD + HO = BZ-CO-O2 + RCO3  
 G31) PF=BZCHO ;BALD + HV + #.05 = #7 XC  
 G32) 1.4E-12, 3.747 ;BALD + NO3 = HNO3 + BZ-CO-O2  
 G33) SAMEK B2 ;BZ-CO-O2 + NO = BZ-O + CO2 + NO2 + R2O2 + RO2  
 G34) 8.4E-12 0.0 0.0 ;BZ-CO-O2 + NO2 = PBZN  
 G36) SAMEK B6 ;BZ-CO-O2 + HO2 = XOOH + CO2 + PHEN  
 G37) SAMEK B9 ;BZ-CO-O2 + RO2 = RO2 + #.5 HO2 + CO2 + PHEN  
 G38) SAMEK B10 ;BZ-CO-O2 + RCO3 = RCO3 + HO2 + CO2 + PHEN  
 G35) 1.6E+15, 25.90 ;PBZN = BZ-CO-O2 + NO2 + RCO3  
 G43) 1.3E-11, -0.596 ;BZ-O + NO2 = NPHE  
 G44) SAMEK B5 ;BZ-O + HO2 = PHEN  
 G45) 1.0E-3 ;BZ-O = PHEN  
 G58) 3.6E-12 ;NPHE + NO3 = HNO3 + BZ(NO2)-O  
 G59) SAMEK G43 ;BZ(NO2)-O + NO2 = #2 XN + #6 XC ! DINITROPHENOL  
 G60) SAMEK B5 ;BZ(NO2)-O + HO2 = NPHE  
 G61) SAMEK G45 ;BZ(NO2)-O = NPHE  
 G7) 1.14E-11 ;HO + AFG1 = HCOCO-O2 + RCO3  
 G8) PF=ACROLEIN ;AFG1 + HV + #.077 = HO2 + HCOCO-O2 + RCO3  
 U2OH) 1.72E-11 ;HO + AFG2 = C2CO-O2 + RCO3  
 U2HV) PF=ACROLEIN ;AFG2 + HV = HO2 + CO + CCO-O2 + RCO3  
 RCH4) 6.255E-13 2.548 2.0 ;CH4 + HO = HCHO + RO2-R + RO2  
 RZ1) 1.0 ;(HCHO2) = #.7 HCOOH + #.12 "HO + HO2 + CO" + &  
       #.18 "H2 + CO2"  
 RZ2) 1.0 ;(CCHO2) = #.25 CCOOH + #.15 "CH4 + CO2" + #.6 HO + &  
       #.3 "CCO-O2 + RCO3" + #.3 "RO2-R + HCHO + CO + &  
       RO2"  
 RZ3) 1.0 ;(RCHO2) = #.25 CCOOH + #.15 CO2 + #.6 HO + &  
       #.3 "C2CO-O2 + RCO3" + #.3 "RO2-R + CCHO + CO + &  
       RO2" + #.55 XC  
 RZ4) 1.0 ;(C(C)CO2) = HO + R2O2 + HCHO + CCO-O2 + RCO3 + RO2  
 RZ5) 1.0 ;(C(R)CO2) = HO + CCO-O2 + CCHO + R2O2 + RCO3 + RO2  
 RZ6) 1.0 ;(CYCCO2) = #.3 "HO + C2CO-O2 + R2O2 + RCO3 + &  
       RO2" + #.3 RCHO + #4.2 XC  
 RZ7) 1.0 ;(BZCHO2) = #.5 "BZ-O + R2O2 + CO + HO"  
 ETOH) 1.960E-12 -0.870 ;ETHE + HO = RO2-R + RO2 + #1.56 HCHO + #.22 CCHO

ETO3) 9.140E-15 5.127 ;ETHE + O3 = HCHO + (HCHO2)  
 ETN3) 5.430E-12 6.043 ;ETHE + NO3 = R2O2 + RO2 + #2 HCHO + NO2  
 ETOA) 1.040E-11 1.574 ;ETHE + O = RO2-R + HO2 + RO2 + HCHO + CO

A1OH) ;HO + ALK1 = #A1OHRR RO2-R + #A1OHNR RO2-N + &  
       #A1OHXN RO2-XN + #A1OHNP RO2-NP + #A1OHRH HO2 + &  
       #A1OHR2 R2O2 + #A1OHRS RO2 + #A1OHA1 HCHO + &  
       #A1OHA2 CCHO + #A1OHA3 RCHO + #A1OK3 ACET + &  
       #A1OK4 MEK + #A1OHCO CO + #A1OHC2 CO2 + &  
       #A1OHPH PHEN + #A1OHCR CRES + #A1OHBZ BALD + &  
       #A1OGL GLY + #A1OHMG MGLY + #A1OHU1 AFG1 + &  
       #A1OHU2 AFG2 + #A1OHTB C2(C)-O + #A1OHQ1 CCO-O2 + &  
       #A1OHQ2 C2CO-O2 + #A1OHQS RCO3 + #A1OHXC XC  
 !

A2OH) ;HO + ALK2 = #A2OHRR RO2-R + #A2OHNR RO2-N + &  
       #A2OHXN RO2-XN + #A2OHNP RO2-NP + #A2OHRH HO2 + &  
       #A2OHR2 R2O2 + #A2OHRS RO2 + #A2OHA1 HCHO + &  
       #A2OHA2 CCHO + #A2OHA3 RCHO + #A2OK3 ACET + &  
       #A2OK4 MEK + #A2OHCO CO + #A2OHC2 CO2 + &  
       #A2OHPH PHEN + #A2OHCR CRES + #A2OHBZ BALD + &  
       #A2OGL GLY + #A2OHMG MGLY + #A2OHU1 AFG1 + &  
       #A2OHU2 AFG2 + #A2OHTB C2(C)-O + #A2OHQ1 CCO-O2 + &  
       #A2OHQ2 C2CO-O2 + #A2OHQS RCO3 + #A2OHXC XC  
 !

B1OH) ;HO + ARO1 = #B1OHRR RO2-R + #B1OHNR RO2-N + &  
       #B1OHXN RO2-XN + #B1OHNP RO2-NP + #B1OHRH HO2 + &  
       #B1OHR2 R2O2 + #B1OHRS RO2 + #B1OHA1 HCHO + &  
       #B1OHA2 CCHO + #B1OHA3 RCHO + #B1OK3 ACET + &  
       #B1OK4 MEK + #B1OHCO CO + #B1OHC2 CO2 + &  
       #B1OHPH PHEN + #B1OHCR CRES + #B1OHBZ BALD + &  
       #B1OGL GLY + #B1OHMG MGLY + #B1OHU1 AFG1 + &  
       #B1OHU2 AFG2 + #B1OHTB C2(C)-O + #B1OHQ1 CCO-O2 + &  
       #B1OHQ2 C2CO-O2 + #B1OHQS RCO3 + #B1OHXC XC  
 !

B2OH) ;HO + ARO2 = #B2OHRR RO2-R + #B2OHNR RO2-N + &  
       #B2OHXN RO2-XN + #B2OHNP RO2-NP + #B2OHRH HO2 + &  
       #B2OHR2 R2O2 + #B2OHRS RO2 + #B2OHA1 HCHO + &  
       #B2OHA2 CCHO + #B2OHA3 RCHO + #B2OK3 ACET + &  
       #B2OK4 MEK + #B2OHCO CO + #B2OHC2 CO2 + &  
       #B2OHPH PHEN + #B2OHCR CRES + #B2OHBZ BALD + &  
       #B2OGL GLY + #B2OHMG MGLY + #B2OHU1 AFG1 + &  
       #B2OHU2 AFG2 + #B2OHTB C2(C)-O + #B2OHQ1 CCO-O2 + &  
       #B2OHQ2 C2CO-O2 + #B2OHQS RCO3 + #B2OHXC XC  
 !

O1OH) ;OLE1 + HO = #O1OHRR RO2-R + #O1OHRN RO2-N + &  
       #O1OHR2 R2O2 + #O1OHA1 HCHO + #O1OHA2 CCHO + &  
       #O1OHA3 RCHO + #O1OK3 ACET + #O1OK4 MEK + &  
       #O1OHBZ BALD + #O1OHXC XC  
 !

O1O3) ;OLE1 + O3 = #O1O3A1 HCHO + #O1O3A2 CCHO + &  
       #O1O3A3 RCHO + #O1O3K3 ACET + #O1O3K4 MEK + &  
       #O1O3BZ BALD + #O1O3Z1 (HCHO2) + #O1O3Z2 (CCHO2) + &  
       #O1O3Z3 (RCHO2) + #O1O3Z4 (C(C)CO2) + &  
       #O1O3Z5 (C(R)CO2) + #O1O3Z6 (CYCCO2) + &  
       #O1O3Z8 (BZCHO2) + #O1O3OH HO + #O1O3RR RO2-R + &  
       #O1O3RN RO2-N + #O1O3XN RO2-XN + #O1O3NP RO2-NP + &

#O1O3RH HO2 + #O1O3R2 R2O2 + #O1O3RS RO2 + &  
 #O1O3Q1 CCO-O2 + #O1O3Q2 C2CO-O2 + #O1O3QS RCO3 + &  
 #O1O3XC XC

!

O1OA) ;OLE1 + O = #O1OARR RO2-R + #O1OARH HO2 + &  
 #O1OARS RO2 + #O1OAA1 HCHO + #O1OAA3 RCHO + &  
 #O1OAK4 MEK + #O1OACO CO + #O1OAXC XC

!

O1N3) ;OLE1 + NO3 = #O1N3N2 NO2 + #O1N3N3 HNO3 + &  
 #O1N3RH HO2 + #O1N3RR RO2-R + #O1N3RN RO2-N + &  
 #O1N3R2 R2O2 + #O1N3RS RO2 + #O1N3A1 HCHO + &  
 #O1N3A2 CCHO + #O1N3A3 RCHO + #O1N3K3 ACET + &  
 #O1N3K4 MEK + #O1N3BZ BALD + #O1N3XC XC

!

O2OH) ;OLE2 + HO = #O2OHRR RO2-R + #O2OHRN RO2-N + &  
 #O2OHRHS RO2 + #O2OHA1 HCHO + #O2OHA2 CCHO + &  
 #O2OHA3 RCHO + #O2OHK3 ACET + #O2OHK4 MEK + &  
 #O2OHBZ BALD + #O2OHXC XC

!

O2O3) ;OLE2 + O3 = #O2O3A1 HCHO + #O2O3A2 CCHO + &  
 #O2O3A3 RCHO + #O2O3K3 ACET + #O2O3K4 MEK + &  
 #O2O3BZ BALD + #O2O3Z1 (HCHO2) + #O2O3Z2 (CCHO2) + &  
 #O2O3Z3 (RCHO2) + #O2O3Z4 (C(C)CO2) + &  
 #O2O3Z5 (C(R)CO2) + #O2O3Z6 (CYCCO2) + &  
 #O2O3Z8 (BZCHO2) + #O2O3OH HO + #O2O3RR RO2-R + &  
 #O2O3RN RO2-N + #O2O3XN RO2-XN + #O2O3NP RO2-NP + &  
 #O2O3RH HO2 + #O2O3R2 R2O2 + #O2O3RS RO2 + &  
 #O2O3Q1 CCO-O2 + #O2O3Q2 C2CO-O2 + #O2O3QS RCO3 + &  
 #O2O3XC XC

!

O2OA) ;OLE2 + O = #O2OARR RO2-R + #O2OARH HO2 + &  
 #O2OARS RO2 + #O2OAA1 HCHO + #O2OAA3 RCHO + &  
 #O2OAK4 MEK + #O2OACO CO + #O2OAXC XC

!

O2N3) ;OLE2 + NO3 = #O2N3N2 NO2 + #O2N3N3 HNO3 + &  
 #O2N3RH HO2 + #O2N3RR RO2-R + #O2N3RN RO2-N + &  
 #O2N3R2 R2O2 + #O2N3RS RO2 + #O2N3A1 HCHO + &  
 #O2N3A2 CCHO + #O2N3A3 RCHO + #O2N3K3 ACET + &  
 #O2N3K4 MEK + #O2N3BZ BALD + #O2N3XC XC

!

O3OH) ;OLE3 + HO = #O3OHRR RO2-R + #O3OHRN RO2-N + &  
 #O3OHRHS RO2 + #O3OHA1 HCHO + #O3OHA2 CCHO + &  
 #O3OHA3 RCHO + #O3OHK3 ACET + #O3OHK4 MEK + &  
 #O3OHBZ BALD + #O3OHXC XC

!

O3O3) ;OLE3 + O3 = #O3O3A1 HCHO + #O3O3A2 CCHO + &  
 #O3O3A3 RCHO + #O3O3K3 ACET + #O3O3K4 MEK + &  
 #O3O3BZ BALD + #O3O3Z1 (HCHO2) + #O3O3Z2 (CCHO2) + &  
 #O3O3Z3 (RCHO2) + #O3O3Z4 (C(C)CO2) + &  
 #O3O3Z5 (C(R)CO2) + #O3O3Z6 (CYCCO2) + &  
 #O3O3Z8 (BZCHO2) + #O3O3OH HO + #O3O3RR RO2-R + &  
 #O3O3RN RO2-N + #O3O3XN RO2-XN + #O3O3NP RO2-NP + &  
 #O3O3RH HO2 + #O3O3R2 R2O2 + #O3O3RS RO2 + &  
 #O3O3Q1 CCO-O2 + #O3O3Q2 C2CO-O2 + #O3O3QS RCO3 + &  
 #O3O3XC XC

!

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O3OA) ;OLE3 + O = #O3OARR RO2-R + #O3OARH HO2 + &
      #O3OARS RO2 + #O3OAA1 HCHO + #O3OAA3 RCHO + &
      #O3OAK4 MEK + #O3OACO CO + #O3OAXC XC
!
O3N3) ;OLE3 + NO3 = #O3N3N2 NO2 + #O3N3N3 HNO3 + &
      #O3N3RH HO2 + #O3N3RR RO2-R + #O3N3RN RO2-N + &
      #O3N3R2 R2O2 + #O3N3RS RO2 + #O3N3A1 HCHO + &
      #O3N3A2 CCHO + #O3N3A3 RCHO + #O3N3K3 ACET + &
      #O3N3K4 MEK + #O3N3BZ BALD + #O3N3XC XC
!
!      END OF FILE

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## Attachment B2 – Listing of Reactions of Isoprene (Condensed 1-Product)

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ISOH) 2.54E-11 -0.81 ;ISOP + HO = #.088 RO2N + #.912 RO2R + &
                      #.629 HCHO + #.912 ISPD + #.079 R2O2 + &
                      #1.079 RO2
!
ISO3) 7.86E-15 3.80 ;ISOP + O3 = #.4 HCHO + #.6 ISPD + #.55 BHCHO2 + &
                      #.2 CC3O2 + #.2 CC3HO2
!
ISOA) 3.60E-11 ;ISOP + O = #.75 ISPD + #.25 "C3O3 + &
                  RCO3 + #2 HCHO + RO2R + RO2"
!
!SOA) 3.60E-11 ;ISOP + O = #.75 "ISPD + XC "+ #.25 "C3O3 + &
                  RCO3 + #2 HCHO + RO2R + RO2"
!
ISN3) 3.03E-12 0.89 ;ISOP + NO3 = #.8 "RCHO + RNO3 + RO2R " + &
                      #.2 "ISPD + R2O2 + NO2" + RO2
!
ISN2) 1.50E-19 ;ISOP + NO2 = #.8 "RCHO + RNO3 + RO2R " + &
                      #.2 "ISPD + R2O2 + NO" + RO2
!
!
IPOH) 3.36E-11 ;ISPD + HO = #.293 CO + #.252 CCHO + #.126 HCHO + &
                  #.041 GLY + #.021 RCHO + #.168 MGLY + #.314 MEK + &
                  #.503 RO2R + #.21 CCO3 + #.288 C3O3 + &
                  #.21 R2O2 + #.713 RO2 + #.498 RCO3
!
IPO3) 7.11E-18 ;ISPD + O3 = #.02 CCHO + #.04 HCHO + #.01 GLY + &
                  #.84 MGLY + #.09 MEK + #.66 BHCHO2 + &
                  #.09 HCOCHO2 + #.18 HOCCHO2 + #.06 C2O2CHO + &
                  #.01 COHC2O2
!
IPHV) PF=ACROLEIN ;ISPD + HV + #.0036 = #.333 CO + #.067 CCHO + &
                  #.9 HCHO + #.033 MEK + #.333 HO2 + #.7 RO2R + &
                  #.267 CCO3 + #.7 C3O3 + #.7 RO2 + &
                  #.967 RCO3
!
IPN3) 1.0E-15 ;ISPD + NO3 = #.643 CO + #.282 HCHO + #.85 RNO3 + &
                  #.357 RCHO + #.925 HO2 + #.075 C3O3 + &

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! #.075 R2O2 + #.925 RO2 + #.075 RCO3 + #.075 HNO3
! #.075 R2O2 + #.925 RO2 + #.075 RCO3 + #.075 HNO3 + &
#2.471 XC
ISZ1) 1.0 ;CC3O2 = HO + R2O2 + HCHO + C3O3 + RO2 + &
RCO3
ISZ2) 1.0 ;CC3HO2 = #.75 RCHO + #.25 ISPD
!ISZ2) 1.0 ;CC3HO2 = #.75 RCHO + #.25 ISPD + #.5 XC
MAZ1) 1.0 ;C2O2CHO = HO + R2O2 + HCHO + HC2O4 + RO2 + &
RCO3
M1Z1) 1.0 ;HOCCHO2 = #.6 HO + #.3 "CCO3 + RCO3" + &
#.3 "RO2R + HCHO + CO + RO2"
#.3 "RO2R + HCHO + CO + RO2" + #.8 XC
;HCOCHO2 = #.12 "HO2 + #2 CO + HO" + &
#.51 HCHO
!M2Z1) 1.0 ;HCOCHO2 = #.12 "HO2 + #2 CO + HO" + #.74 XC + &
#.51 "CO2 + HCHO"
M2Z2) 1.0 ;COHC2O2 = HO + MGLY + HO2 + R2O2 + RO2
!      END OF FILE

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### Attachment B3 – Listing of Explicit Reaction Mechanisms for Other VOCs

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OH001) 2.500E-12 0.397 0.000 ;C6H6 + HO = #.236 PHEN + #.207 GLY &
+ #1.44 AFG1 + #.764 RO2-R + #.236 HO2 &
+ #1.29 XC + #.764 RO2
!
OH033) 1.480E-11 -0.890 0.000 ;BUTD + HO = RO2-R + RO2 + HCHO + RCHO
!
O3033) 1.340E-14 4.537 0.000 ;BUTD + O3 = #.6 HCHO + RCHO + #1.2 XC &
+ #.4 (HCHO2) + #.6 (CCHO2)
!
N3033) 1.000E-13 0.000 0.000 ;BUTD + NO3 = R2O2 + RO2 + HCHO + RCHO &
+ NO2
!
OA033) 2.100E-11 0.000 0.000 ;BUTD + O = #.4 HO2 + #.5 RCHO + #.5 MEK &
+ #.5 XC
!
OH018) 3.840E-13 0.000 0.000 ;PDCB + HO = #.236 PHEN + #.207 GLY &
+ #1.44 AFG1 + #.764 RO2-R + #.236 HO2 &
+ #1.29 XC + #.764 RO2
!
OH152) 9.640E-12 2.403 0.000 ;PERC + HO = RO2-R + CCHO + RO2
!
OH086) 6.14E-18 1.987 2.000 ;DICM + HO = RO2-R + HCHO + RO2
!
AS1) 6.14E-25 ; AS = AS
CR1) 6.14E-25 ; CRVI = CRVI
!
C1) PF=HCHONEWR ;FORM + HV = #2 HO2 + CO
C2) PF=HCHONEWM ;FORM + HV = H2 + CO

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C3) 1.125E-12 -1.288 2.0 ;FORM + HO = HO<sub>2</sub> + CO + H<sub>2</sub>O  
C4) 9.7E-15, -1.242 ;FORM + HO<sub>2</sub> = HOCOO  
C9) 2.8E-12, 5.00 ;FORM + NO<sub>3</sub> = HNO<sub>3</sub> + HO<sub>2</sub> + CO  
!  
C10) 5.55E-12, -0.618 ;ALD + HO = CCO-O<sub>2</sub> + H<sub>2</sub>O + RCO<sub>3</sub>  
C11A) PF=CCHOR ;ALD + HV = CO + HO<sub>2</sub> + HCHO + RO<sub>2</sub>-R + RO<sub>2</sub>  
C12) 1.4E-12, 3.696 ;ALD + NO<sub>3</sub> = HNO<sub>3</sub> + CCO-O<sub>2</sub> + RCO<sub>3</sub>  
!  
OH091) 5.560E-13 -1.057 2.000 ;ETOH + HO = #.1 RO<sub>2</sub>-R + #.9 HO<sub>2</sub> &  
+ #.156 HCHO + #.922 CCHO + #.1 RO<sub>2</sub>  
!  
OH108) 6.129E-13 -0.914 2.000 ;MTBE + HO = #.02 RO<sub>2</sub>-N + #.98 RO<sub>2</sub>-R &  
+ #.37 R<sub>2</sub>O<sub>2</sub> + #.39 HCHO + #.41 MEK + #2.87 XC &  
+ #1.37 RO<sub>2</sub>  
! END OF FILE